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Structural Ceramics

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NASA Lewis Research Center
Cleveland, Ohio
May 20-21, 1986*

NASA

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National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

1986

PREFACE

Welcome to Lewis Research Center and the Materials Division. We are very pleased that you could visit us and hear about all the progress we, our contractors, and grantees have been making in ceramics. We feel ceramics and ceramic matrix composites are an exciting area of tailored structural materials research. NASA has made a strong commitment to advance this technology and we will work with U.S. industry to foster our national position in world markets. In fact, that is the job of the Materials Division in all areas of NASA technology needs.

If any of your organizations are interested in more detailed information on our programs, in joint research efforts, or in sending a research here for some extended on-site studies, feel free to call me and we will discuss it.

Sal Grisaffe

Chief, Materials Division

(216) 433-3193

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CERAMICS FOR TURBINE ENGINES

Stanley R. Levine

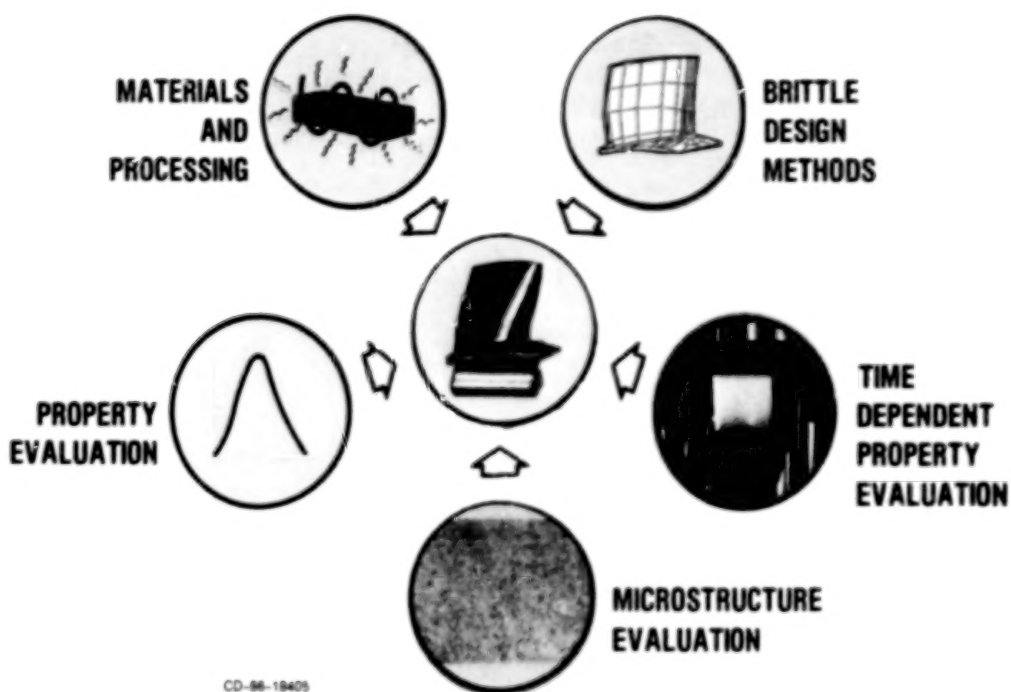
NASA Lewis Research Center
Cleveland, Ohio 44135

The Ceramics for Turbine Engines Project is comprised of three main research thrusts with major elements as indicated:

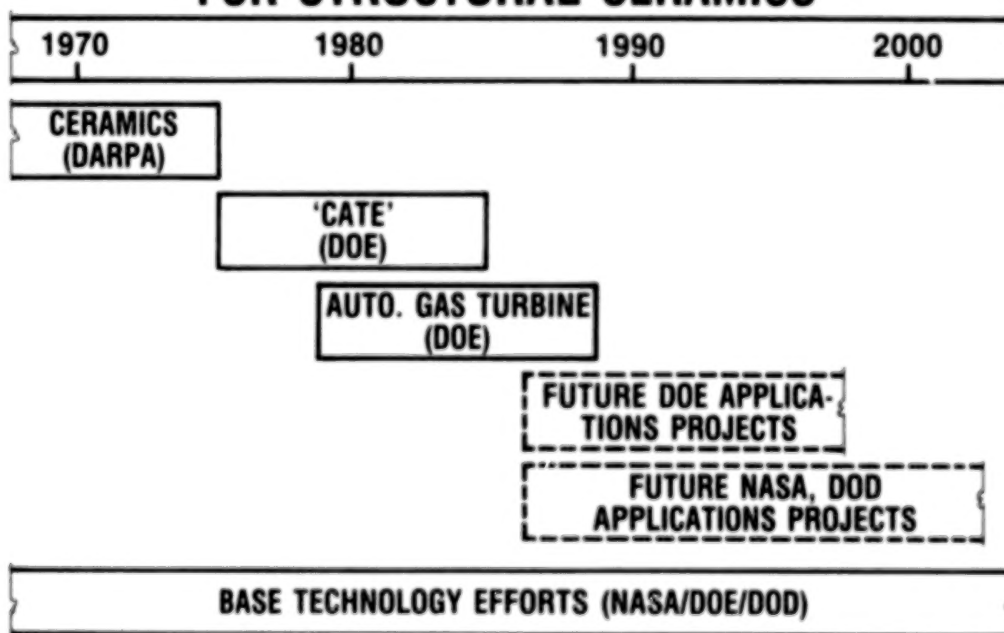
- Materials and Processing
 - Monolithics
 - Fiber reinforced
- Design Methodology
 - Design code
 - Tribology
- Life Prediction
 - Environmental effects
 - Non-destructive evaluation
 - Fracture and fatigue
 - Time dependent behavior

The overall objective of this program is to provide the ceramics technology base in materials and structures for aerospace propulsion and power applications programs. The effort is complementary to and coordinated with the Department of Energy funded Ceramic Technology for Advanced Heat Engines Project at Oak Ridge National Laboratory. From the NASA perspective an enhanced ceramics technology base directly supports aeronautics initiatives in small engine technology, high-performance turbine engine technology, and hypersonics. The Ceramics for Turbine Engines Project is funded at about \$2M per year and involves about 20 researchers in the Materials Division and the Structures Division at Lewis as well as contract and grant research. An overview of the program, which includes the technical objectives and content of each thrust, is provided in the following figures. This workshop reports on research efforts funded mainly by Ceramics for Turbine Engines. A major strength of the program is the increasingly interdisciplinary nature of the research being carried out in-house. Several of the papers presented will illustrate and demonstrate the benefits of such an approach.

CERAMICS FOR TURBINE ENGINES



GOVERNMENT-SPONSORED TECHNOLOGY PROGRAMS FOR STRUCTURAL CERAMICS



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DOE/NASA ADVANCED GAS TURBINE TECHNOLOGY DEVELOPMENT PROJECT

OBJECTIVE

- DEVELOP A TECHNOLOGY BASE APPLICABLE TO A COMPETITIVE AUTOMOTIVE GAS TURBINE ENGINE

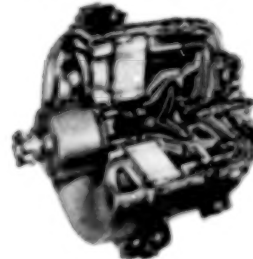
TECHNOLOGY DEVELOPMENT GOALS

- 30% IMPROVEMENT IN FUEL ECONOMY OVER A CONVENTIONAL (SI) ENGINE IN A 3000 LB VEHICLE
- ADAPTABILITY TO ALTERNATIVE FUELS
- MEET OR EXCEED PRESENT EMISSION STANDARDS
- COMPETITIVE RELIABILITY, LIFE, AND COSTS

APPROACH

- TWO ENGINE/AUTOMOBILE CONTRACTOR TEAMS (GARRETT/FORD AND ALLISON/PONTIAC)
- DESIGN, FABRICATE, AND TEST ALL-CERAMIC HOT SECTION COMPONENTS
- SUPPORTING RESEARCH AND TECHNOLOGY EFFORT IN CRITICAL AREAS
- INITIATED 1980-PLANNED COMPLETION 1986

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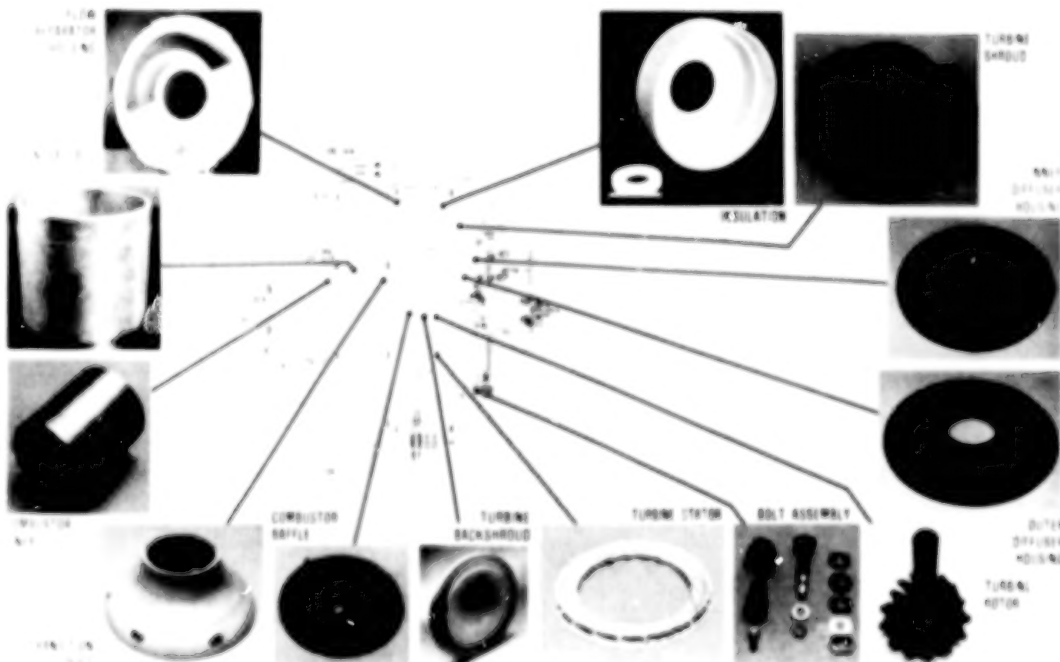


AGT-101

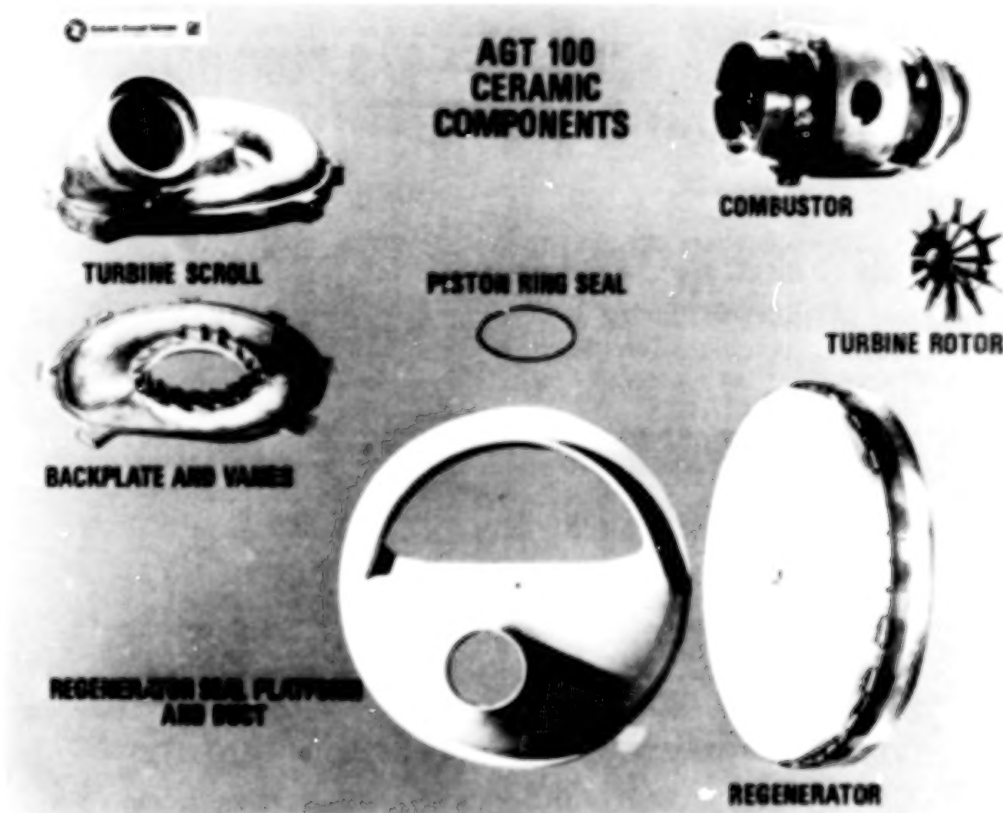


AGT-100

AGT101 CERAMIC COMPONENTS



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STATUS OF MONOLITHIC CERAMIC MATERIALS

CERAMIC MATERIALS HAVE DEMONSTRATED:

- ★ GOOD HIGH TEMPERATURE STRENGTH
- ★ GOOD OXIDATION RESISTANCE
- ★ GOOD EROSION RESISTANCE
- ★ NET SHAPE FABRICATION CAPABILITY

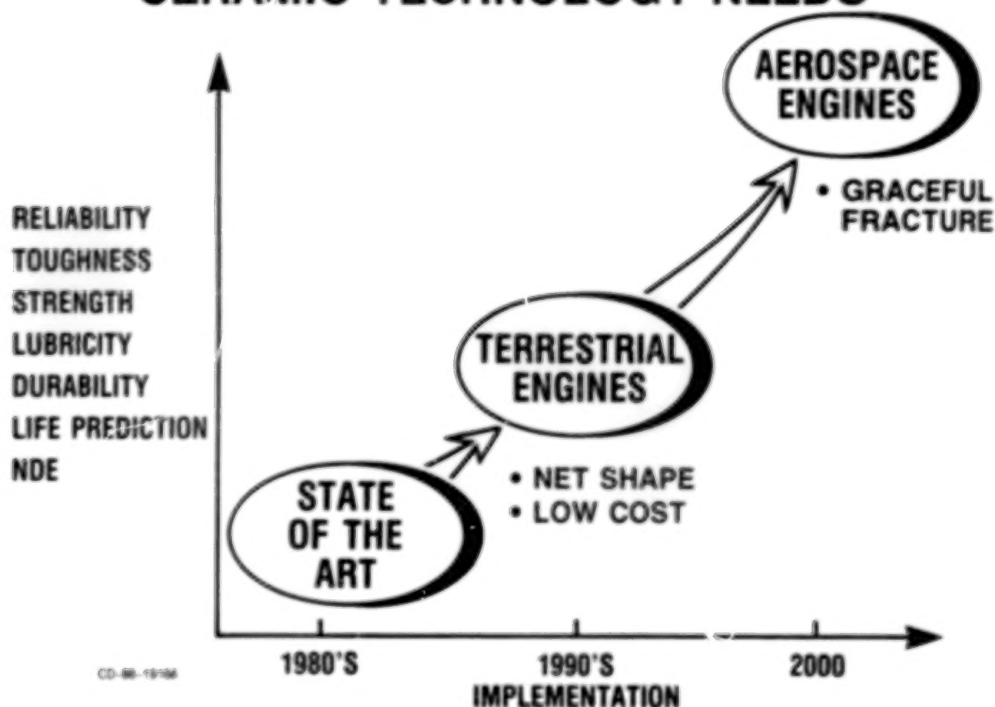
BUT

- ★ LOW RELIABILITY



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CERAMIC TECHNOLOGY NEEDS



STRATEGIC THRUSTS IN AERONAUTICS TO ESTABLISH TECHNOLOGY FOR 21st CENTURY ADVANCED AIRCRAFT

NASA OAST/AERONAUTICS - NOVEMBER 1984

PRESIDENTIAL SCIENCE ADVISOR KEYWORD - APRIL 1985

- DEVELOP ESSENTIAL TECHNOLOGIES FOR HIGH-EFFICIENCY SUBSONIC TRANSPORTS.
- ESTABLISH TECHNOLOGY READINESS FOR EFFICIENT SUPERSONIC CRUISE TRANSPORT AND FIGHTER/ATTACK AIRCRAFT.
- DEVELOP ESSENTIAL TECHNOLOGIES FOR REALIZATION OF PRACTICAL HYPERSONIC AND TRANSATMOSPHERIC FLIGHT AIRCRAFT.

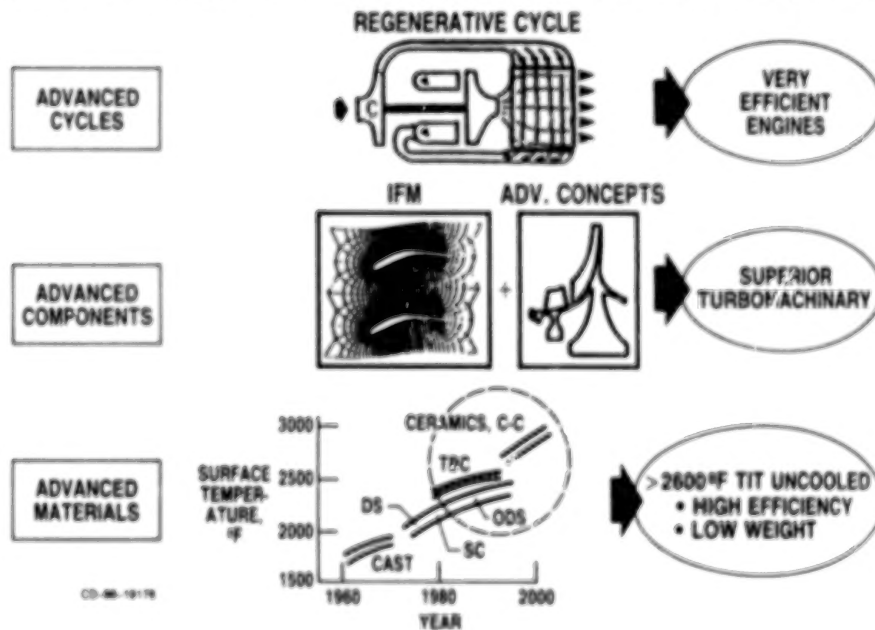
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FUTURE OPPORTUNITIES IN AEROPROPULSION PROPULSION SYSTEMS			
	1990's	2000's	2010's
SUBSONICS	 ATP  VERY-HIGH BYPASS ENGINE  CONVERTIBLE ROTORCRAFT ENGINE  ADV. SMALL TURBINE ENGINE  ROTARY ENGINE		 BEAM POWER
SUPERSONICS	 HIGH-T/W SUPERSONIC ENGINE  SUPERSONIC STOVL ENGINE	 VARIABLE-CYCLE ENGINE	
HYPERSONICS/ TRANSATMOSPHERICS	 TURBORAMJET  AIR-TURBORAMJET	 ADV CONCEPTS	CD-85-18043

Lewis Research Center

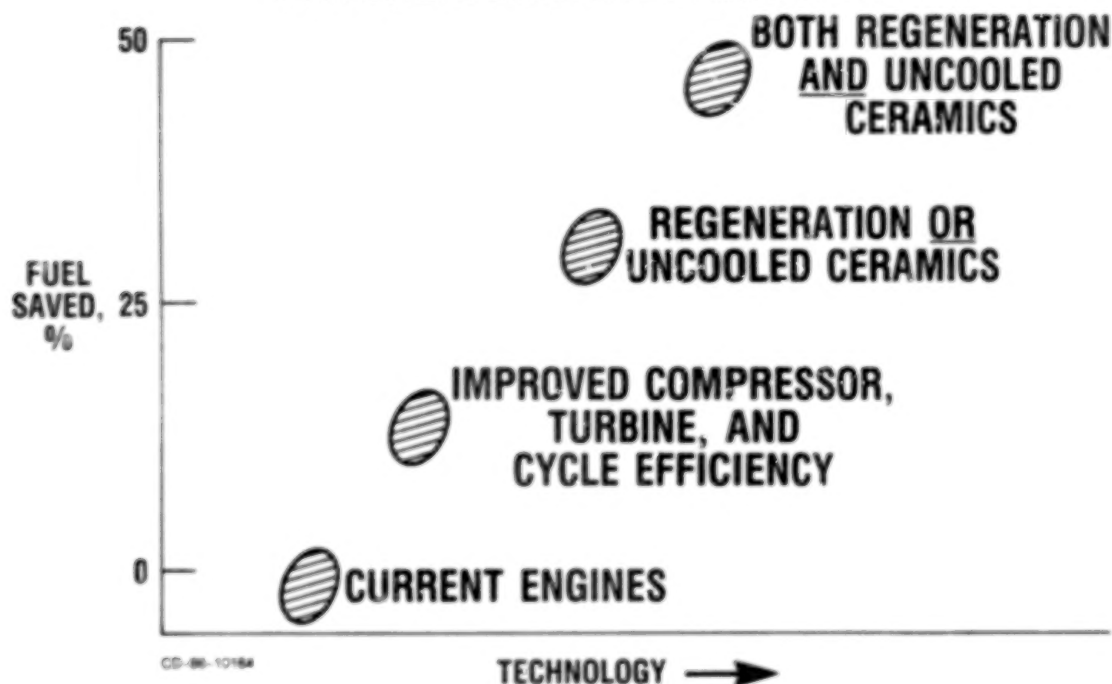
NASA

SMALL ENGINE TECHNOLOGY OPPORTUNITIES



TECHNOLOGY BENEFITS FROM CERAMICS

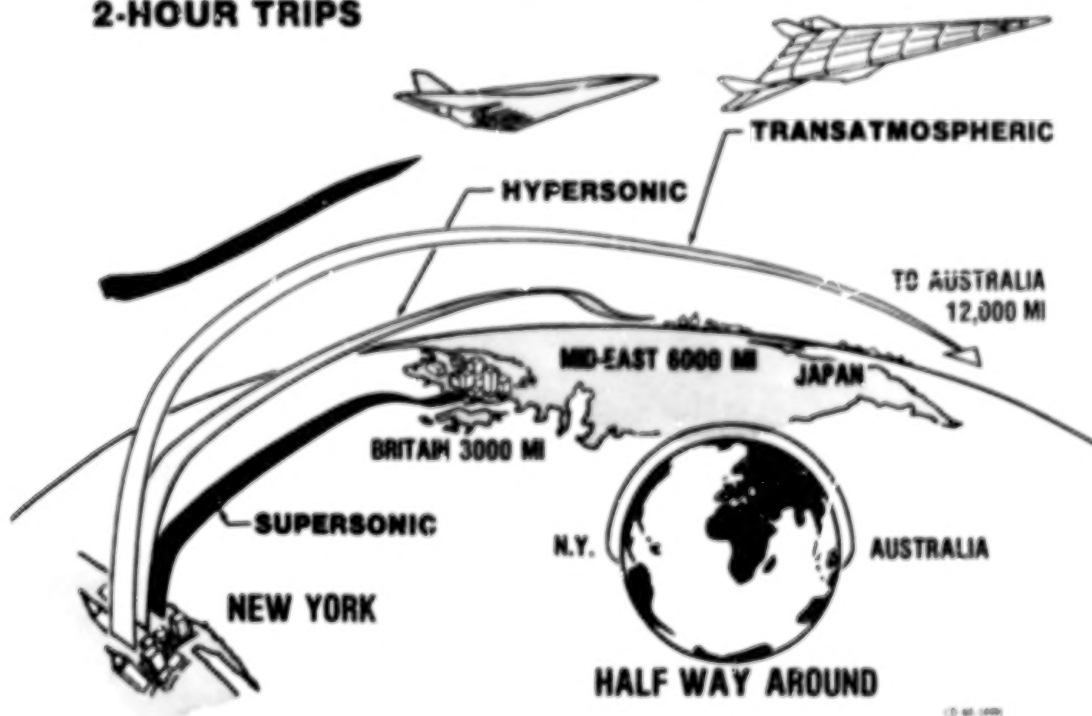
TYPICAL-COMMUTER MISSION



Lewis Research Center

NASA

FUTURE HIGH-SPEED AIR TRANSPORTATION 2-HOUR TRIPS



CERAMICS FOR TURBINE ENGINES

OBJECTIVE

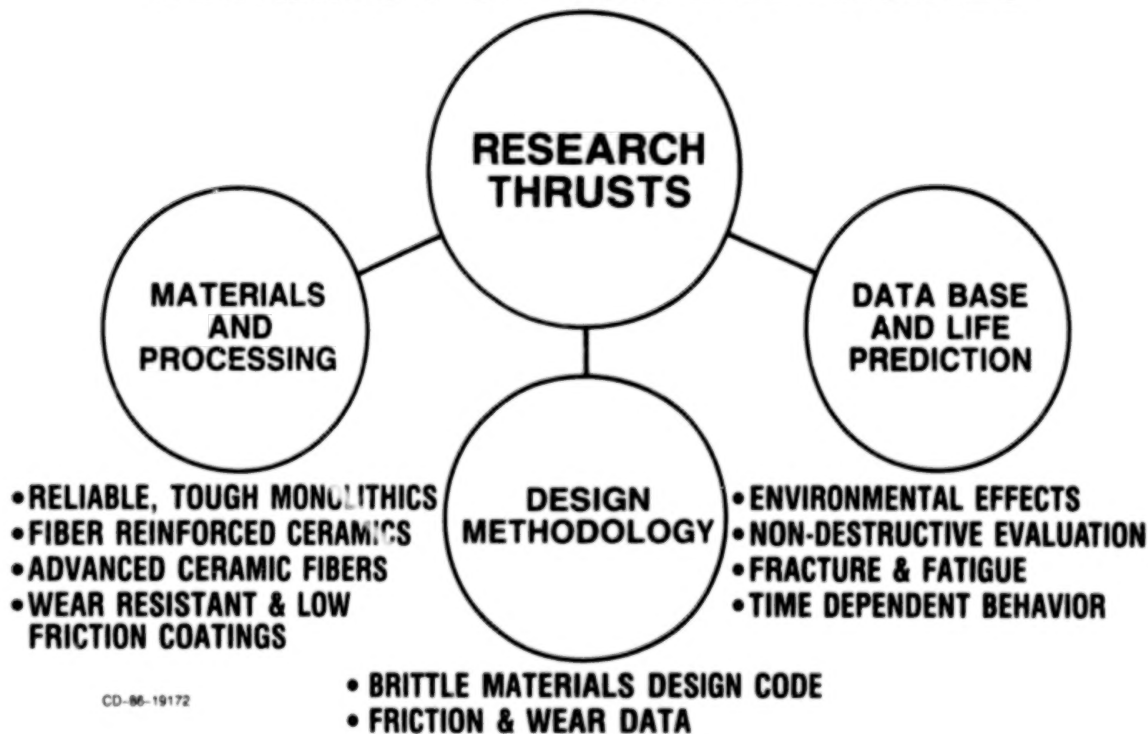
DEVELOP THE TECHNOLOGY
REQUIRED TO IMPROVE STRUCTURAL
CERAMIC RELIABILITY AND PERMIT
USE OF CERAMICS IN ADVANCED
HEAT ENGINES



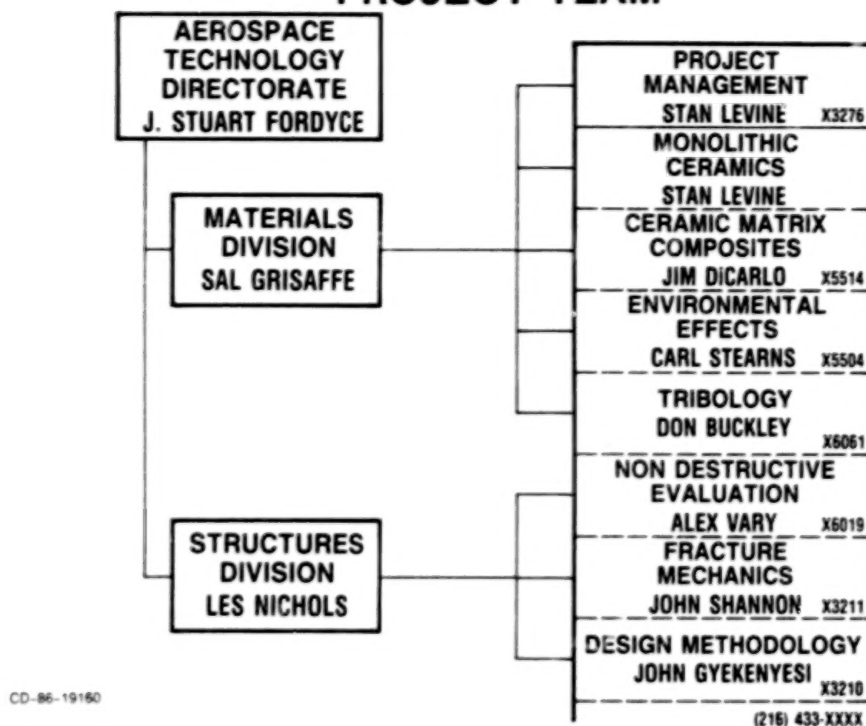
APPROACHES

- MATERIALS AND PROCESSING
- DESIGN METHODOLOGY
- LIFE PREDICTION

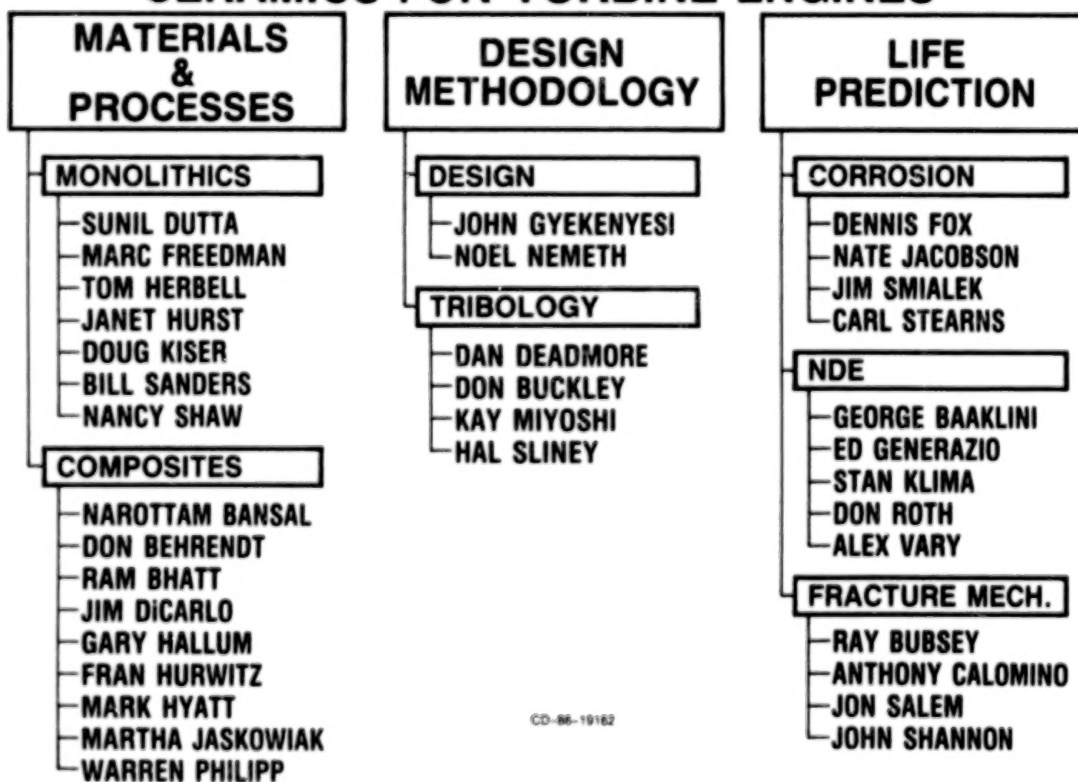
CERAMICS FOR TURBINE ENGINES



CERAMICS FOR TURBINE ENGINES PROJECT TEAM



CERAMICS FOR TURBINE ENGINES



LEWIS CERAMICS CAPABILITIES

FIBERS

FIBER COATING
HIGH TEMPERATURE FIBER TESTING
FIBER PHYSICAL/MECHANICAL PROPERTIES

CERAMIC/CERAMIC COMPOSITE FABRICATION

FIBER/MATRIX TAPE FAB
HOT PRESS
REACTION BONDING
HOT ISOSTATIC PRESS (2200 °C, 20 ksi)
HIGH PRESSURE N₂ SINTERING (2150 °C, 1000 psi)
CVD & CVI FABRICATION
SOL GEL PROCESSING/CHARACTERIZATION
POLYMER PROCESSING/CHARACTERIZATION
POWDER PROCESSING/CHARACTERIZATION

INTERDISCIPLINARY COLLABORATION

ENVIRONMENTAL EFFECTS - BURNER RIGS, H₂/O₂ RIG, COATINGS
NDE - RADIOGRAPHY ACOUSTIC MICROSCOPY, ULTRASONICS
FRACTURE MECHANICS & FATIGUE
STRUCTURAL ANALYSIS & DESIGN METHODOLOGY
SURFACE SCIENCE - FRICTION, WEAR, COATINGS

CD 86-1948

CERAMICS FOR TURBINE ENGINES

—MATERIALS AND PROCESSING—

OBJECTIVE:

IMPROVE RELIABILITY, STRENGTH AND TOUGHNESS OF CERAMICS/CERAMIC MATRIX COMPOSITES

APPROACH: POWDER DERIVED MATERIALS



POWDER PROCESSING



SINTERING

STRONGER,
TOUGHER CERAMICS

IMPROVE
RELIABILITY

CHEMICALLY DERIVED MATERIALS

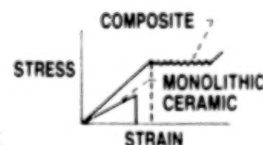


MICROSTRUCTURE

CONTROLLED PROPERTIES
MICROSTRUCTURES & MODELS

QUANTIFY PROGRESS
& DEFINE NEW OPTIONS

COMPOSITES



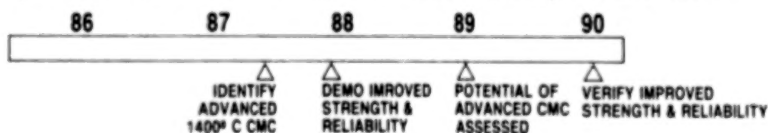
FIBER REINFORCED
CERAMICS

IMPROVE STRENGTH,
TOUGHNESS & PROVIDE
GRACEFUL FRACTURE

BENEFITS:

ADVANCED CERAMIC MATERIALS TECHNOLOGY FOR AEROSPACE PROPULSION AND POWER APPLICATIONS (E.G. ADVANCED SMALL ENGINE TECHNOLOGY (ASET), HYPERSONICS)

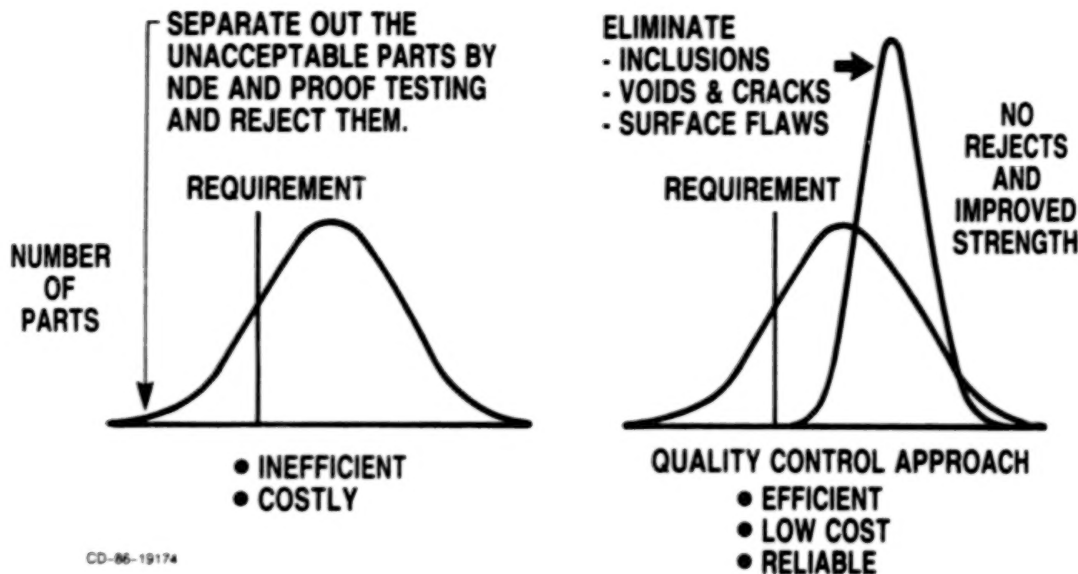
SCHEDULE:



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APPROACHES TO CERAMIC RELIABILITY

"INSPECT-IN" THE QUALITY IMPROVE THE PROCESS



MONOLITHIC CERAMICS

OBJECTIVES:

- UNDERSTAND MICROSTRUCTURE/PROCESSING/PROPERTIES/RELATIONSHIPS
- IMPROVE RELIABILITY

APPROACHES

SINTERING/HIGH P_{N_2}



SINTERED Si_3N_4 (SSN)

REACTION BONDED
 Si_3N_4 (RBSN)

SINTERED REACTION
BONDED Si_3N_4 (SRBSN)

SINTERED SiC (SSC)

HIP



CD-86-19178

FIBER REINFORCED CERAMICS APPROACH TO RELIABILITY

INCORPORATE CONTINUOUS CERAMIC FILAMENTS HAVING
GREATER STIFFNESS THAN MATRIX

• ADVANTAGES

- IMPROVED TOUGHNESS IMPARTED BY CRACK DEFLECTION
AND CRACK BRIDGING
- INCREASED MODULUS AND STRESS TO FAILURE
- "METAL-LIKE" STRESS-STRAIN BEHAVIOR
- GRACEFUL FAILURE

• DISADVANTAGES

- PROCESSING MORE DIFFICULT
- AVAILABLE FIBERS LIMITED
- CONTROL OF FIBER-MATRIX BOND REQUIRED

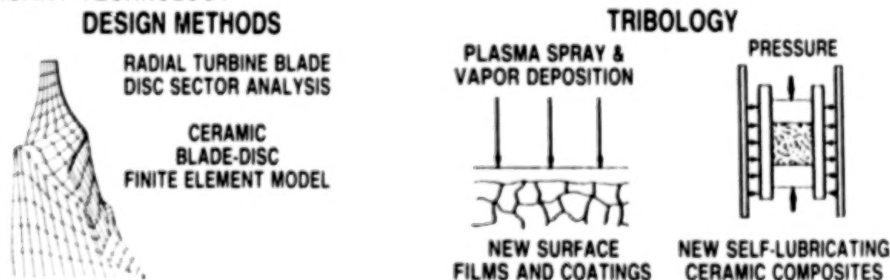
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CERAMICS FOR TURBINE ENGINES —DESIGN METHODOLOGY—

OBJECTIVES:

- DEVELOP AND VERIFY MECHANICAL DESIGN METHODS FOR CERAMIC AND CERAMIC COMPOSITE COMPONENTS
- UNDERSTAND FRICTION/WEAR INTERACTIONS AND DEVELOP HIGH TEMPERATURE SOLID FILM AND COMPOSITE LUBRICANT TECHNOLOGY

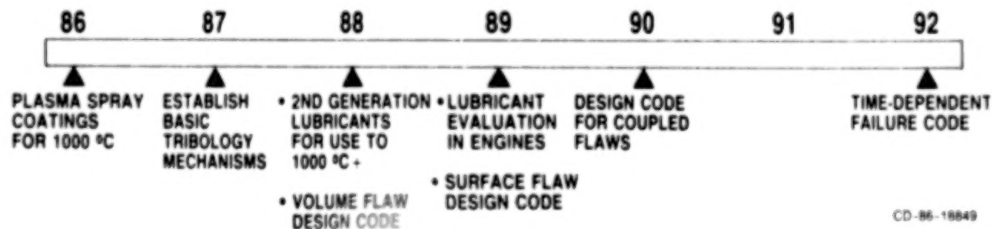
APPROACH:



BENEFITS:

ENABLING TECHNOLOGY TO PERMIT USE OF CERAMIC MATERIALS IN ADVANCED AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE: AT GL



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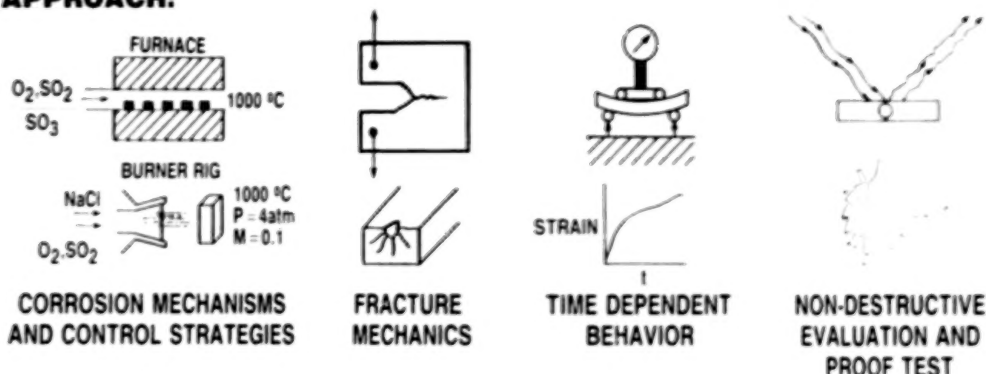
CERAMICS FOR TURBINE ENGINES

—LIFE PREDICTION—

OBJECTIVE:

DEVELOP LIFE PREDICTION AND RELIABILITY ASSESSMENT TOOLS FOR STRUCTURAL CERAMICS

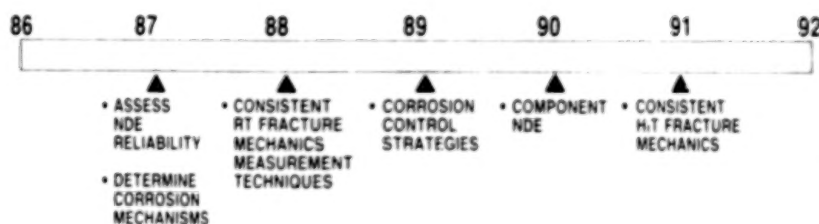
APPROACH:



BENEFITS:

- ENABLING TECHNOLOGY TO PERMIT RELIABLE DESIGN AND USE OF ADVANCED CERAMIC MATERIALS
- GUIDE DEVELOPMENT OF DURABLE CERAMICS FOR AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE:



CD-86-19169

FUTURE OPPORTUNITIES FOR CERAMICS

SYSTEMS

- VEHICULAR AND STATIONARY POWER
- ADVANCED SMALL ENGINE TECHNOLOGY (ASET)
- HIGH-THRUST-TO-WEIGHT ENGINES (HPTE)
- AEROSPACEPLANE

MATERIAL NEEDS

- HIGH-TEMPERATURE, NON-STRATEGIC MATERIALS AT LOW COST (2500 °F)
- VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (2700 °F)
- ADVANCED RECUPERATORS/REGENERATORS (2200 °F)
- ASSEMBLY OF CERAMICS INTO A WORKABLE ENGINE SYSTEM
- VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (3000 °F)
- SAME AS HPTE (3000 °F + +)
- DURABLE CERAMICS FOR USE IN 0° AT HIGH HEAT FLUX (EDGE INSERTS) AND IN H₂/O₂ (ENGINE SEALS)

OPPORTUNITY

- CONTINUE EMPHASIS ON RELIABILITY
- DEVELOP THERMALLY STABLE 10 TO 25 μ DIAMETER CERAMIC FIBER AND APPLY IN CERAMIC MATRIX COMPOSITES
- DEVELOP AND VERIFY POTENTIAL OF ADVANCED MATERIALS
- ADVANCED JOINING, NONJOINING AND CONTACT STRESS CONTROL TECHNOLOGY
- DESIGN AND LIFE PREDICTION
- FIBERS AND COMPOSITES
- FIBERS AND COMPOSITES
- IDENTIFY SUITABLE MATERIALS

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N88-23874

FRICTION AND WEAR OF CERAMICS

Donald H. Buckley ✓
NASA Lewis Research Center

The adhesion, friction, wear, and lubricated behaviors of both oxide and non-oxide ceramics are reviewed. Ceramics are examined in contact with themselves, other harder materials, and metals. Elastic, plastic, and fracture behavior of ceramics in solid state contact is discussed. The contact load necessary to initiate fracture in ceramics is shown to be appreciably reduced with tangential motion. Both friction and wear of ceramics are anisotropic and relate to crystal structure as with metals. Grit size effects in two- and three-body abrasive wear are observed for ceramics. Both the free energy of oxide formation and the d valence bond character of metals are related to the friction and wear characteristics for metals in contact with ceramics. Surface contaminants affect friction and adhesive wear. For example, carbon on silicon carbide and chlorine on aluminum oxide reduce friction while oxygen on metal surfaces in contact with ceramics increases friction. Lubrication increases the critical load necessary to initiate fracture of ceramics both in indentation and with sliding or rubbing.

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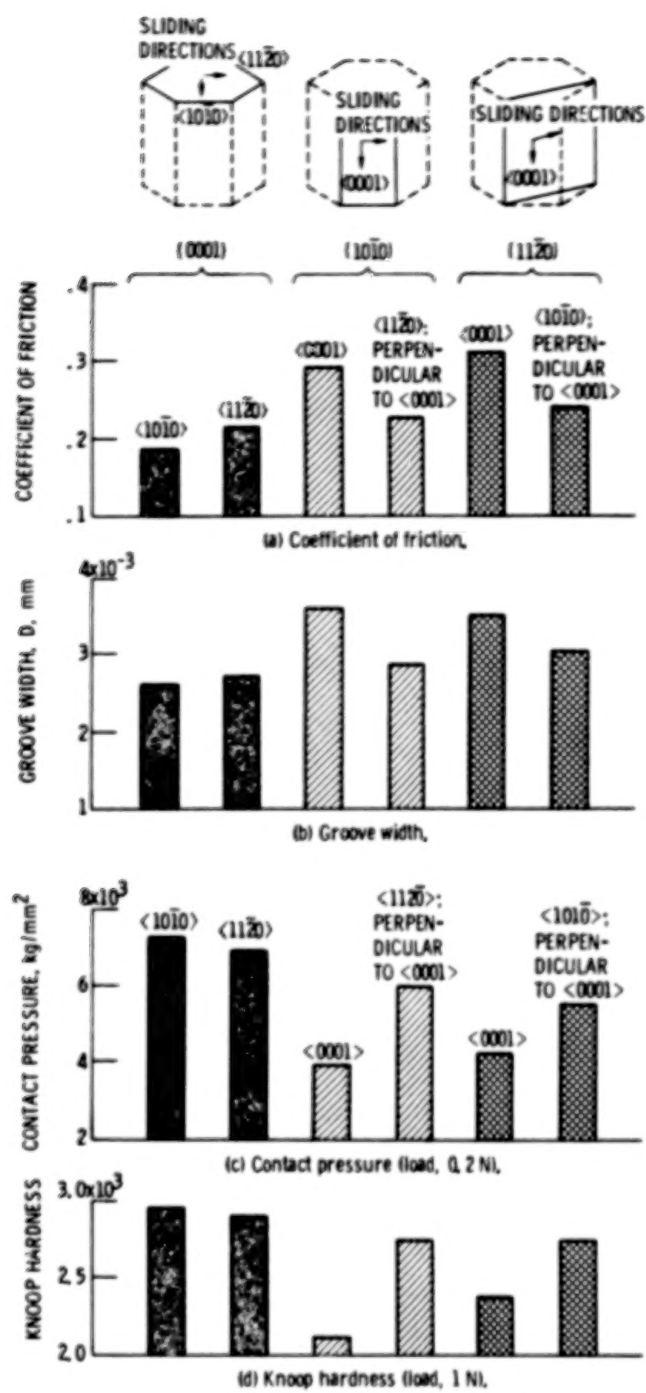


Figure 1. - Anisotropies on (0001) , $(10\bar{1}0)$, and $(11\bar{2}0)$ surfaces of SiC.

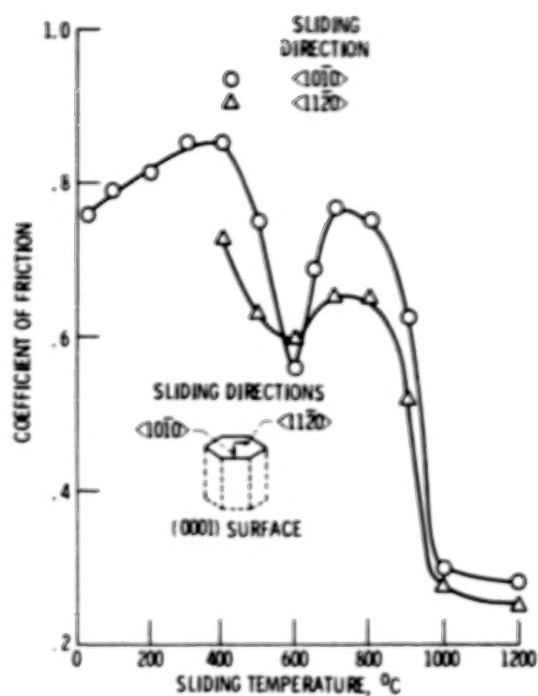


Figure 2. - Effect of temperature on coefficient of friction for silicon carbide [0001] surface sliding against an iron rider. The iron rider was argon ion sputter cleaned before experiments. Normal load, 0.2 N, vacuum, 10^{-6} Pa.

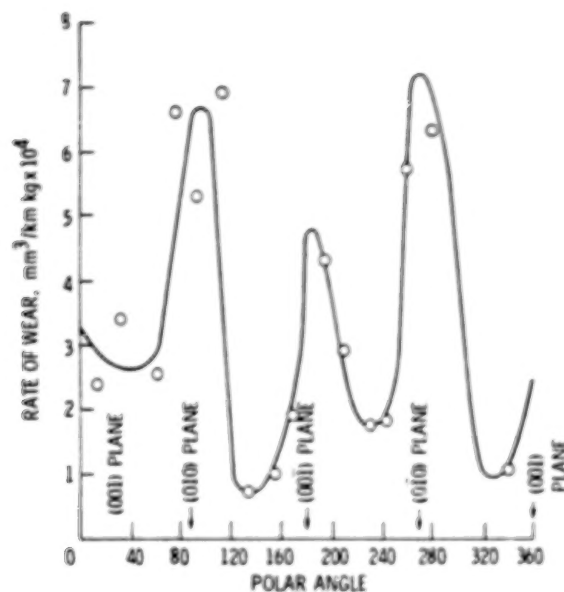


Figure 3. - Rate of wear of a rutile single-crystal sphere on a great circle in the plane of the a- and c-axes is normal to plane of sliding at 0 and 180°. Slide direction in plane of the great circle (ref. 8).

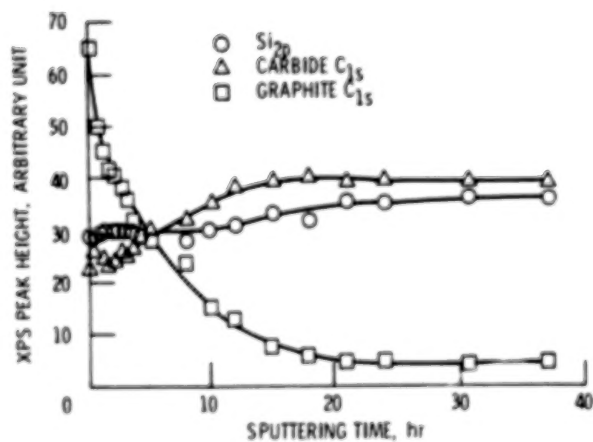


Figure 4. - Elemental depth profile of silicon carbide [0001] surface preheated a temperature of 1500°C for 1 hour.

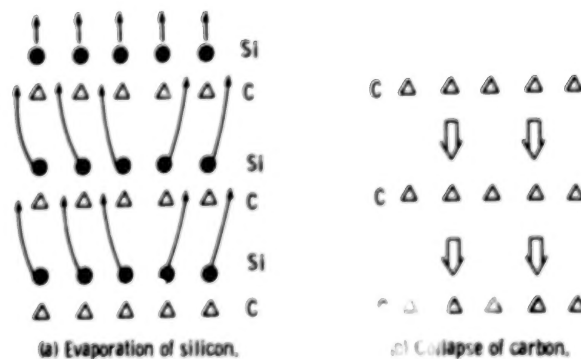


Figure 5. - Graphitization of silicon carbide surface.

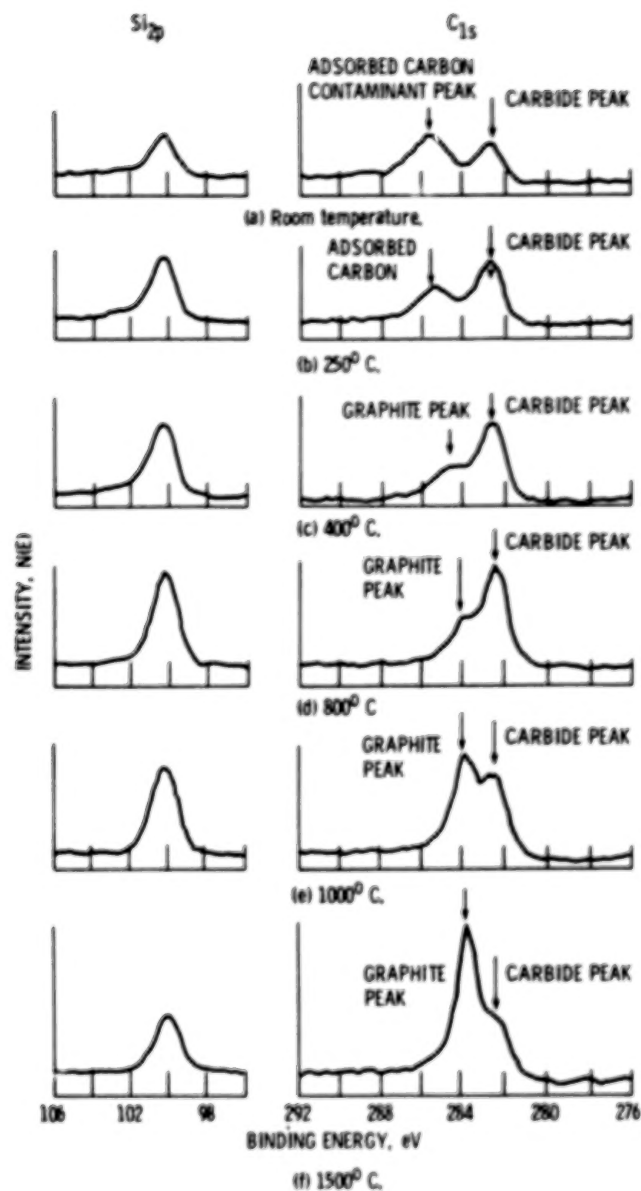


Figure 6. - Representative Si_{2p} and C_{1s} XPS peaks on silicon carbide (1000) surface preheated at various temperatures to 1500°C .

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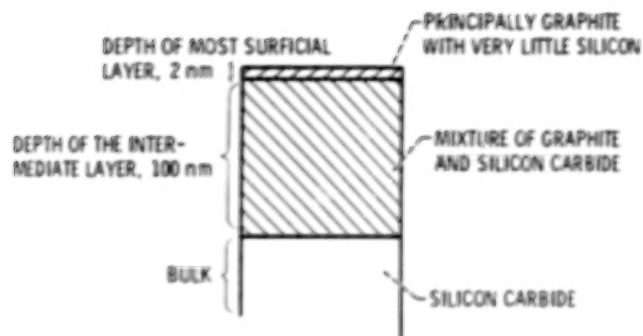


Figure 7. - Surface condition of silicon carbide after heating at temperatures above 1200° C.

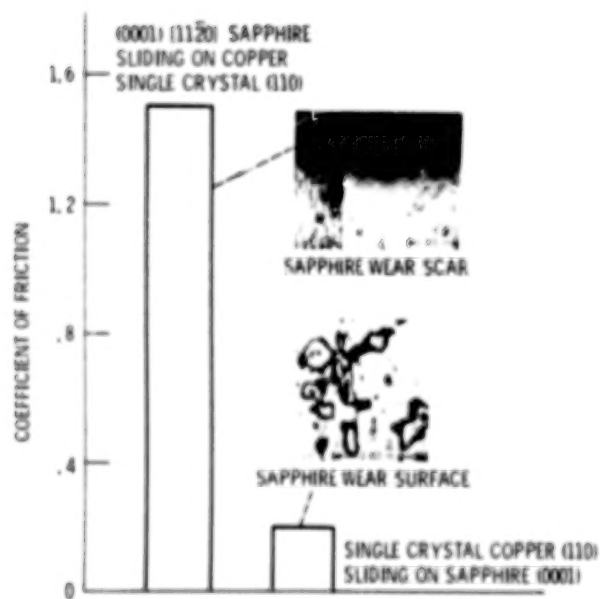


Figure 8. - Friction for copper in sliding contact with sapphire in vacuum 30 mPa; load, 100 g; sliding velocity, 0.013 cm/s.

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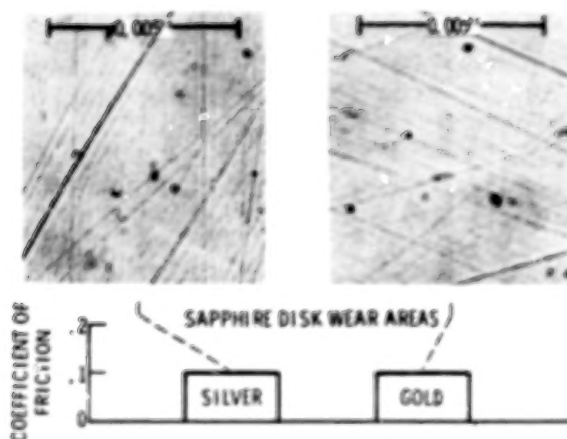


Figure 9. - Coefficient of friction for gold and silver riders sliding on sapphire in vacuum (30 nPa). Sliding velocity, 0.013 cm/s; ambient temperature, 25°C; duration, 1hr.

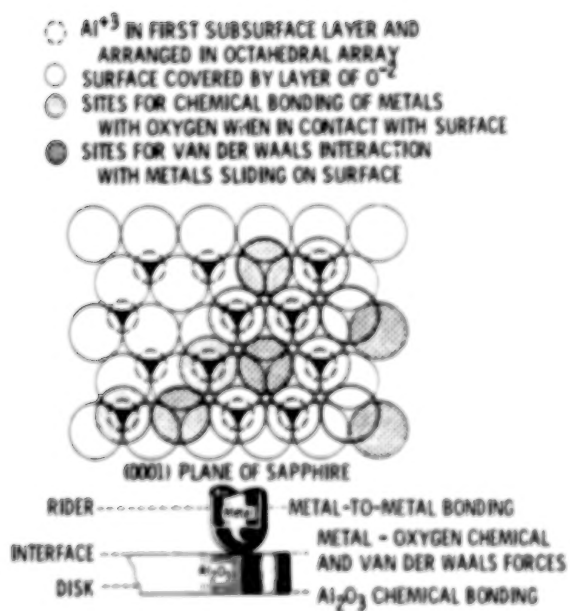


Figure 10. - Nature of surface interaction and bonding of metal to Al_2O_3

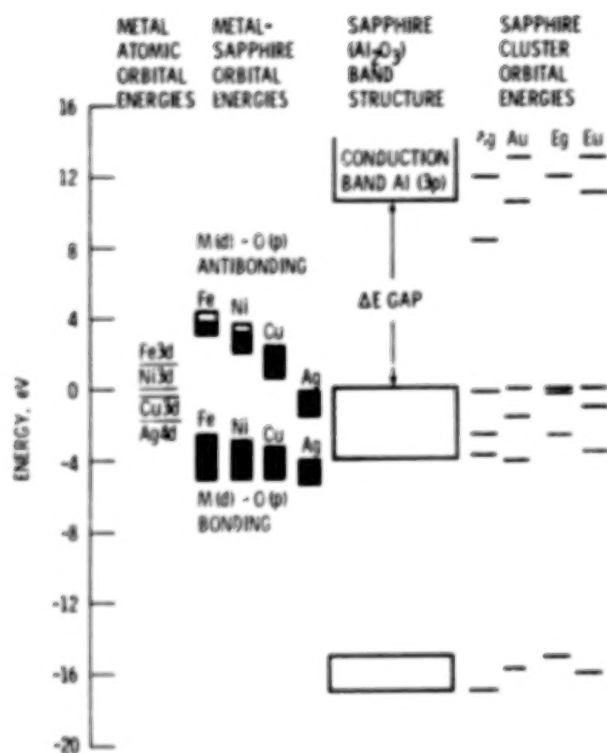
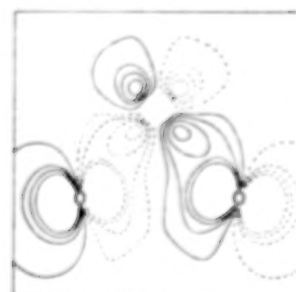
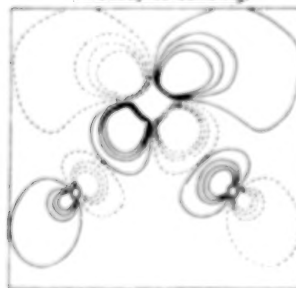


Figure 11. - Molecular-orbital energies, as determined by the self-consistent-field X-alpha scattered wave method, for clusters representing bulk sapphire and metal-sapphire interfaces



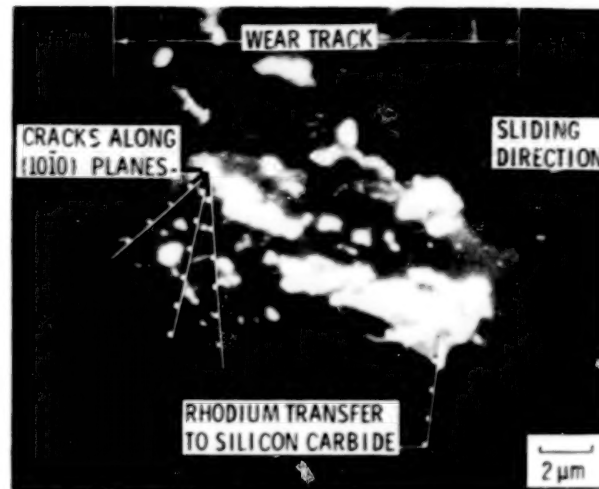
(a) Occupied bonding.



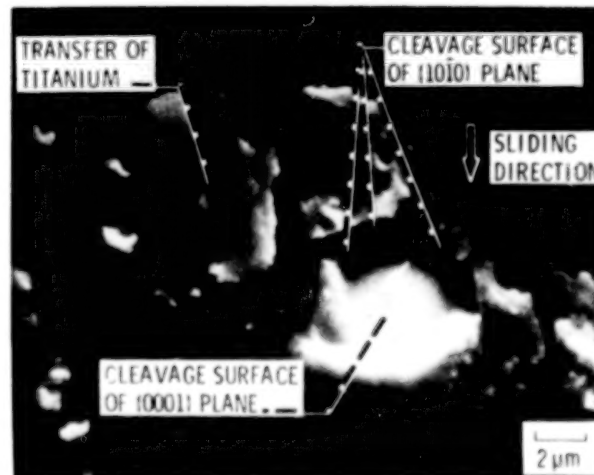
(b) Unoccupied antibonding.

Figure 12. - Fe(d) - O(p) molecular-orbital wave-function contour maps for an iron atom supported on sapphire, plotted in the plane of the iron atom and two surface oxygen atoms. The solid and dashed contours represent the positive and negative phases of the wave function

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(a) Hexagonal cracking.



(b) Hexagonal pit.

Figure 13. - Scanning electron photomicrographs of wear tracks on the (0001) surface of single-crystal SiC in contact with rhodium and titanium as a result of ten passes of a rider in vacuum. Sliding direction, $\langle 10\bar{1}0 \rangle$; sliding velocity, 3 mm/min^{-1} ; load, 0.3 N ; room temperature; pressure, 30 nPa ; metal pin rider, 0.79 mm radius.

SOME DESIGN CONSIDERATIONS FOR CERAMIC COMPONENTS IN HEAT ENGINE APPLICATIONS

John P. Gyekenyesi
NASA Lewis Research Center
Cleveland, Ohio 44135

This presentation reviews the design methodology for brittle material structures which is being developed and used at the Lewis Research Center for sizing ceramic components in heat engine applications. Theoretical aspects of designing with structural ceramics are discussed, and a general purpose reliability program for predicting fast fracture response due to volume distributed flaws is described. Statistical treatment of brittle behavior, based on the Weibull model, is reviewed and its advantages, as well as drawbacks, are listed. A mechanistic statistical fracture theory, proposed by Batdorf to overcome the Weibull model limitations and based on Griffith fracture mechanics, is summarized. Failure probability predictions are made for rotating annular Si_3N_4 disks using various fracture models, and the results are compared to actual failure data. The application of these design methods to Government funded ceramics engine demonstration programs is surveyed. The uncertainty in observed component performance emphasizes the need for proof testing and improved NDE technology to guarantee adequate structural integrity.

POSSIBLE APPROACHES TO CERAMIC DESIGN

A. PROTOTYPE TESTING

- NO STRESS ANALYSIS REQUIRED
- POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
- EVERY DESIGN IS UNIQUE
- EXPENSIVE

B. SCALE MODEL EVALUATION

- VOLUME EFFECT MUST BE INCLUDED
- NO MECHANICAL STRESS ANALYSIS NEEDED
- POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
- THERMAL STRESS PROBLEM CANNOT BE SCALED
- EVERY DESIGN IS UNIQUE
- LESS EXPENSIVE

C. USE OF TEST SPECIMEN TESTING

- VOLUME EFFECT MUST BE INCLUDED
- FULL THERMOMECHANICAL ANALYSIS REQUIRED
- COMBINED FRACTURE STRESS THEORY NEEDED
- CAN BE APPLIED TO ALL DESIGNS
- INEXPENSIVE

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POTENTIAL FAILURE MODES IN HEAT ENGINES

A. TIME INDEPENDENT FAILURE MODES

- FAST FRACTURE (TENSION-COMPRESSION)
- BUCKLING

B. TIME DEPENDENT FAILURE MODES

- STATIC FATIGUE
- DYNAMIC FATIGUE
- CREEP CRACK GROWTH
- STRESS CORROSION AND OXIDATION
- IMPACT AND DYNAMIC LOADING

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SCHEMATICS OF STRENGTH TESTS



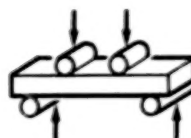
UNIAXIAL TENSILE STRENGTH



HYDROSTATIC TENSILE



3-POINT BENDING



4-POINT BENDING



UNIAXIAL COMPRESSIVE



DIAMETRAL COMPRESSION

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BRITTLE MATERIAL DESIGN METHOD

MATERIAL BRITTLENESS AND PRESENCE OF MICROCRACKS REQUIRES

- ALLOWANCE FOR STRENGTH DISPERSION - PROBABILISTIC APPROACH
- CONSIDERATION OF MATERIAL VOLUME UNDER STRESS (COMBINATION OF STRESS AND VOLUME DETERMINE INTEGRITY)
- REFINED THERMAL AND STRESS ANALYSIS - FIELD SOLUTIONS (EXAMINATION OF CRITICAL POINT IS NOT ADEQUATE)

DESIGN PRACTICE

- FAILURE MODE IS FRACTURE DUE TO CRACK PROPAGATION
- PROOF TESTING AND/OR NDE REQUIRED TO TRUNCATE STRENGTH DISTRIBUTION - ESTABLISH ALLOWABLE STRESS
- NO DESIGN CODES AND ONLY LIMITED EXPERIENCE AVAILABLE

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FRACTURE THEORIES

I. GRIFFITH (1920 AND 1924)

- CRACK SHAPE, SIZE, ORIENTATION SPECIFIED
- IGNORES VOLUME EFFECT
- USES MECHANISTIC FRACTURE CRITERION
- APPROACH IS DETERMINISTIC (BASIS FOR LEFM)

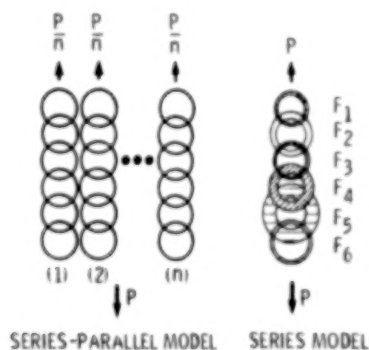
II. WEIBULL (1939)

- CRACK SHAPE, SIZE, ORIENTATION NOT SPECIFIED
- INCLUDES ALLOWANCE FOR STRENGTH DISPERSION
- EXPLAINS VOLUME EFFECT
- USES EMPIRICAL FRACTURE CRITERION
- APPROACH IS PROBABILISTIC

STATISTICAL TREATMENTS

WEAKEST LINK THEORY FOR TENSILE LOADING

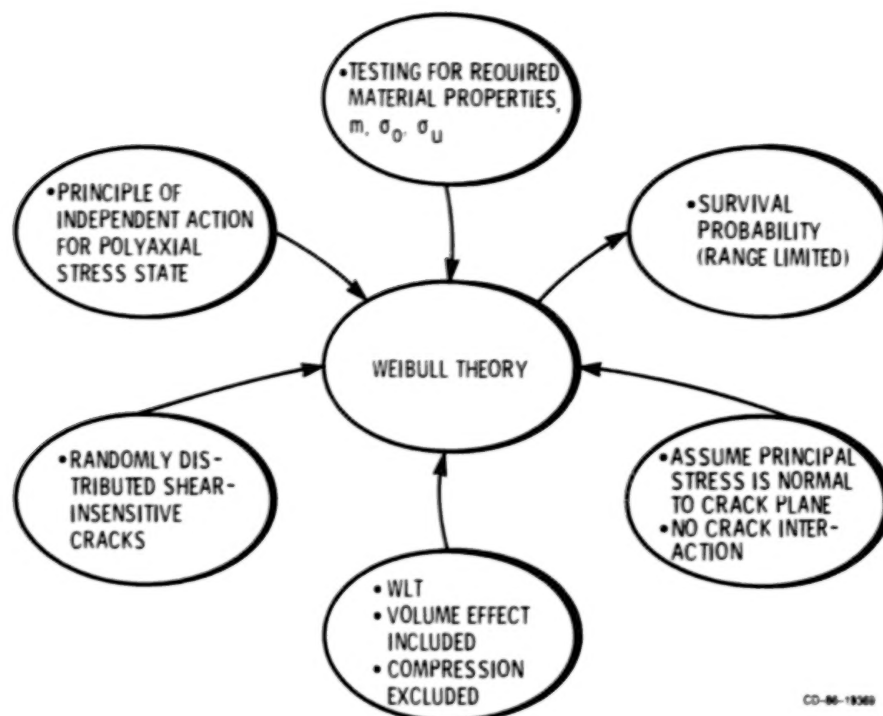
- MATERIAL CONTAINS N FLAWS OR LINKS
- EACH FLAW OR LINK HAS A σ_{cr}
- UPON SINGLE LINK FAILURE, TWO REDISTRIBUTION MECHANISMS ARE POSSIBLE



- STRUCTURAL CERAMICS ARE ASSUMED TO FOLLOW THE SERIES MODEL
- FAILURE OF SINGLE LINK IMPLIES COMPONENT FAILURE, NO CRACK ARREST MECHANISM EXISTS

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ELEMENTS OF WEIBULL'S THEORY (1)



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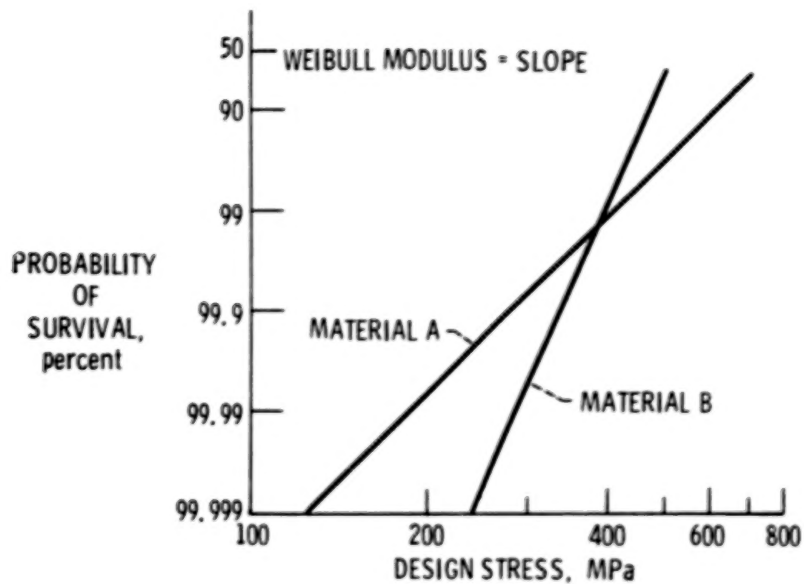
WEIBULL THEORY (2) (CONTINUED)

SURVIVAL PROBABILITY	EQUATION
IN UNIAXIAL TENSION	$P_S(\sigma) = P_S^V(\sigma) \cdot P_S^A(\sigma)$
DUE TO VOLUME CRACKS	$P_S^V(\sigma) = \exp \left[- \int_V \left(\frac{\sigma - \sigma_U^V}{\sigma_0^V} \right)^{m_V} dv \right]$
DUE TO SURFACE CRACKS	$P_S^A(\sigma) = \exp \left[- \int_A \left(\frac{\sigma - \sigma_U^A}{\sigma_0^A} \right)^{m_A} dA \right]$
IN POLYAXIAL TENSION	$P_S(\sigma_1, \sigma_2, \sigma_3) = P_S(\sigma_1) \cdot P_S(\sigma_2) \cdot P_S(\sigma_3)$

WHERE σ = APPLIED STRESS AND $\sigma_1, \sigma_2, \sigma_3$ = PRINCIPAL STRESSES.

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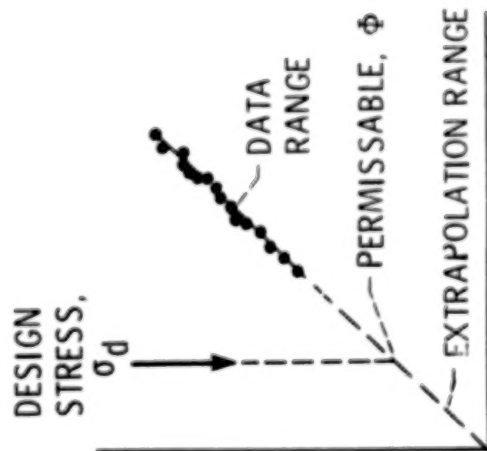
HYPOTHETICAL EXAMPLE OF IMPORTANCE OF HIGH WEIBULL MODULUS FOR STRUCTURAL CERAMICS



ADVANTAGES OF PROBABILISTIC DESIGN

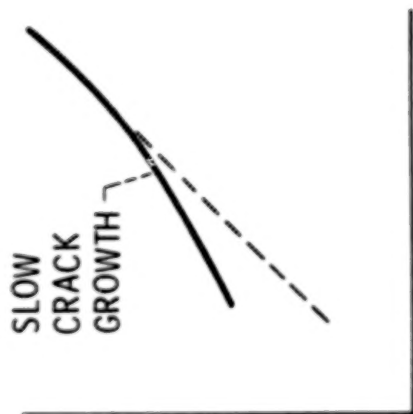
- PERMITS EFFICIENT MATERIAL UTILIZATION
- INCLUDES TRADE-OFF BETWEEN HIGH STRENGTH AND LOW SCATTER
- ACCOUNTS FOR MATERIAL STRENGTH DISPERSION
- INCLUDES COMPONENT SIZE EFFECT

LIMITATIONS OF THE DIRECT STATISTICAL APPROACH

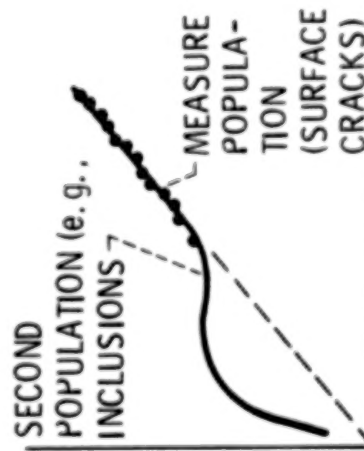


BASIC DATA

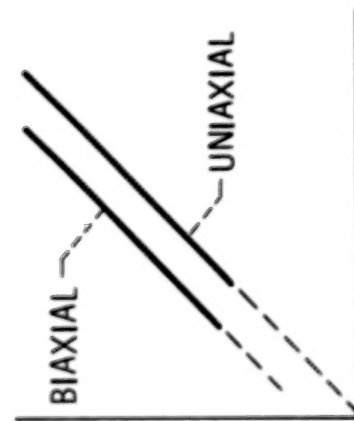
$-\ln(1 - \phi)$



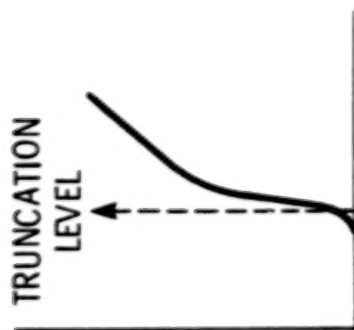
EFFECTS OF SLOW CRACK GROWTH



UNDETECTED FLAW POPULATIONS

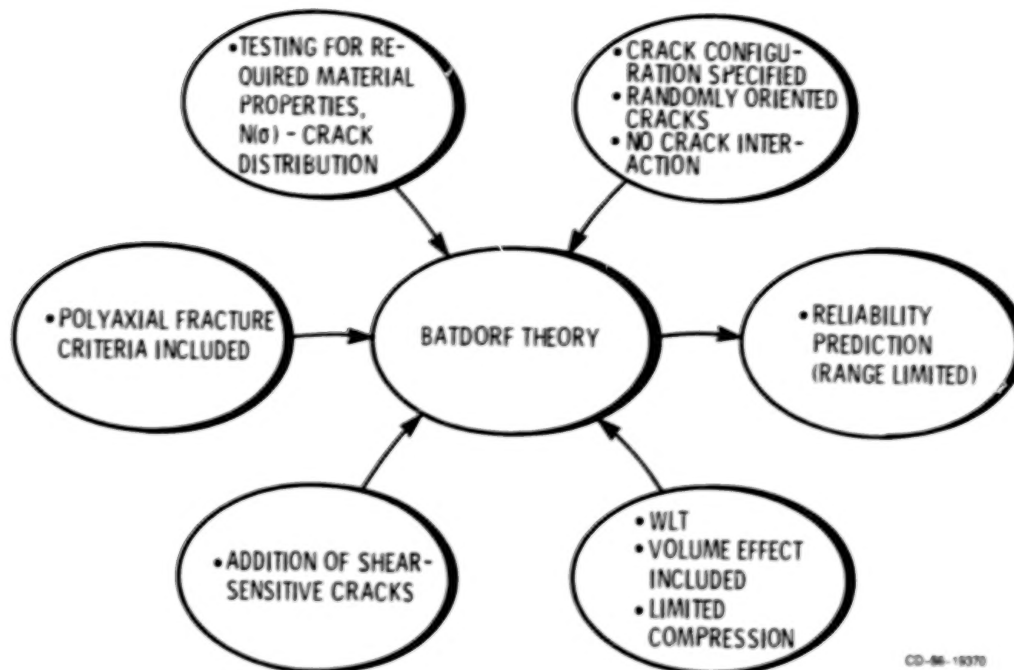


STRESS STATE EFFECTS



TRUNCATION PROCEDURES

ELEMENTS OF BATDORF'S THEORY (1)



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BATDORF THEORY (2) (CONTINUED)

$$P_S(\Sigma) = P_S^V \cdot P_S^A$$

$$P_S^V = \exp \left(- \int_0^{\sigma_1} \int_0^{\sigma_1} \frac{\Omega}{4\pi} \frac{dN_1}{d\sigma_{cr}} d\sigma_{cr} dv \right)$$

$$P_S^A = \exp \left(- \int_0^{\sigma_1} \int_0^{\sigma_1} \frac{u}{\pi} \frac{dN_2}{d\sigma_{cr}} d\sigma_{cr} dA \right)$$

$$N_1 = K_1 \sigma_{cr}^{m_1}$$

$$N_2 = K_2 \sigma_{cr}^{m_2}$$

$$u = f_1(\sigma_{cr}, \sigma_1, \sigma_2)$$

$$\Omega = f_2(\sigma_{cr}, \sigma_1, \sigma_2, \sigma_3, \alpha)$$

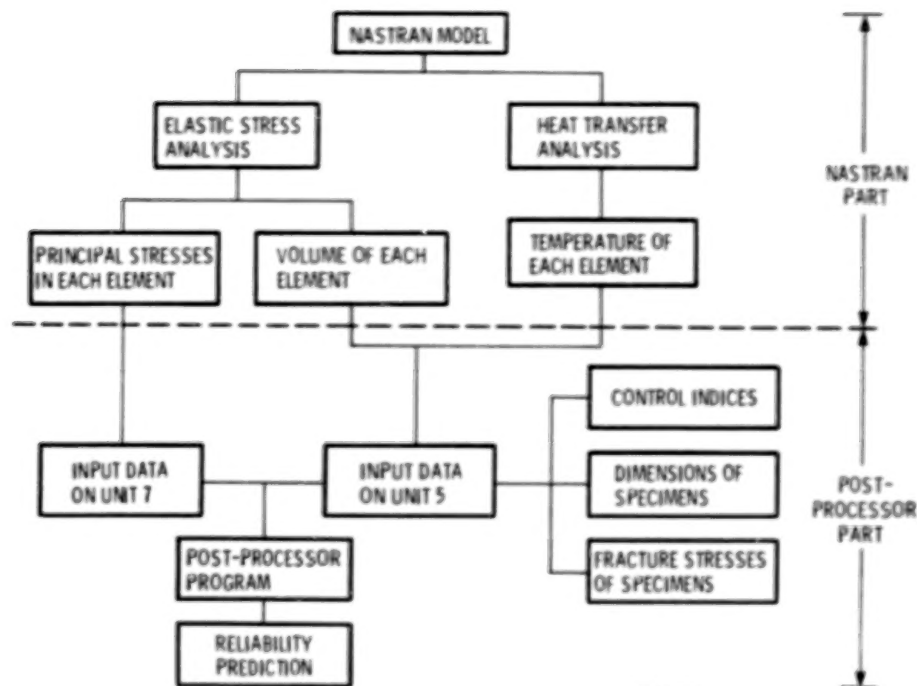
$$\sigma_e = f_3(\sigma_n, \tau), f_3 \text{ DEPENDS UPON THE FRACTURE CRITERION SELECTED}$$

$$\sigma_n = f_4(\sigma_1, \sigma_2, \sigma_3, \alpha, \beta)$$

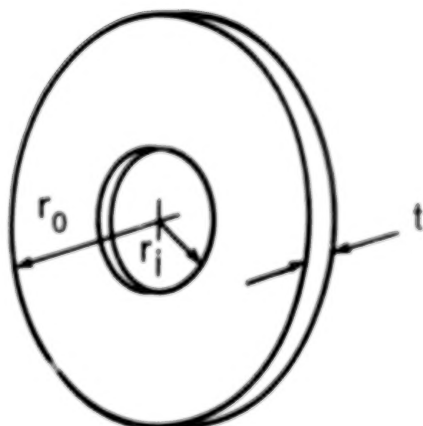
$$\tau = f_5(\sigma_1, \sigma_2, \sigma_3, \alpha, \beta)$$

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FLOW CHART FOR RELIABILITY PREDICTION (VOLUME FLAWS ONLY)



EXAMPLE 1 - ROTATING ANNULAR DISK



DATA:

NC - 132 HOT PRESSED Si_3N_4

$m = 7.65$

$\sigma_0 = 74.82 \text{ MPa } m^{-.3922}$

$\bar{k}_B = 16.30$

$r_i = 6.35 \text{ mm } (.25 \text{ in})$

$r_o = 41.275 \text{ mm } (1.625 \text{ in})$

$t = 3.80 \text{ mm } (.15 \text{ in})$

RPM RANGE - 70K TO 114K

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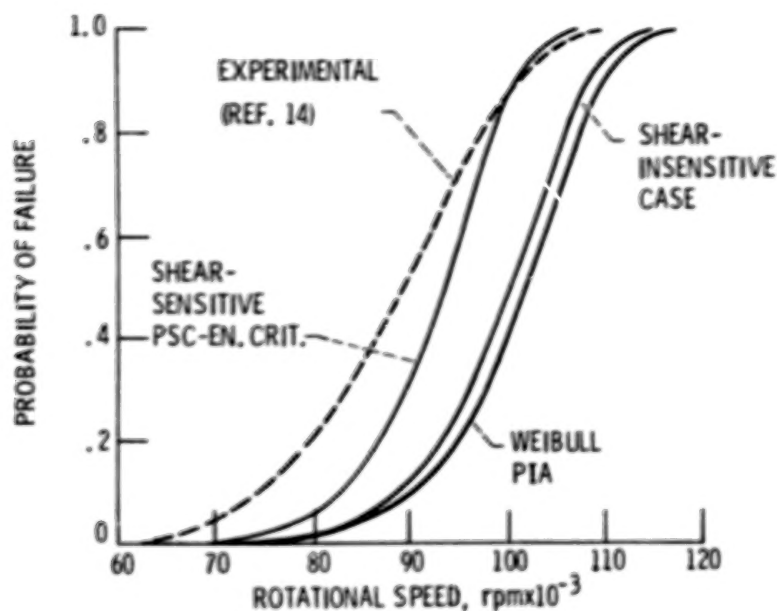


Fig. 7 Example 1 probability of failure vs disk rotational speed for various fracture models (SCARE2 data).

APPLICATION TO CERAMICS

- INITIALLY ONLY WEIBULL THEORY WAS USED (INCLUDES CATE, AGT, AND DARPA PROGRAMS)
- LIMITED SUCCESS AND ACCURACY OBTAINED
- BATDORF BRIDGES GAP BETWEEN FRACTURE THEORIES IN 1974 (GRAPHITE NOSE CONES)
- UNIVERSITY OF WASHINGTON (UW) APPLIES BATDORF'S THEORY TO CERAMICS (NASA GRANT)
- LeRC CORRECTS UW PUBLICATIONS AND DEVELOPS GENERAL PURPOSE DESIGN PROGRAM - SCARE
- SCARE INCLUDES WEIBULL AND BATDORF THEORIES
- SCARE RELEASED TO GM, FORD, TRW, BOEING, GE, AND NASA AND ARMY FOR INITIAL EVALUATION

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RADIAL TURBINE BLADE DISC SECTOR ANALYSIS

**CERAMIC
BLADE - DISC
FINITE ELEMENT MODEL**

CONCLUSIONS

1. PROBABILISTIC DESIGN APPROACH AND WLT MUST BE USED FOR CERAMICS
2. FRACTURE MECHANICS MUST BE APPLIED TO IMPROVE MODELING OF:
 - MULTI-AXIALITY EFFECT
 - DELAYED FAILURE
3. PROOF-TESTING AND/OR NDE SHOULD BE USED TO AVOID DATA EXTRAPOLATION
4. MULTIPLE FLAW DISTRIBUTIONS SHOULD BE INCLUDED IN THE ANALYSIS
5. IMPROVED FRACTURE TOUGHNESS AND MATERIAL PROCESSING ARE NEEDED TO INCREASE CERAMIC STRENGTH

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P-12

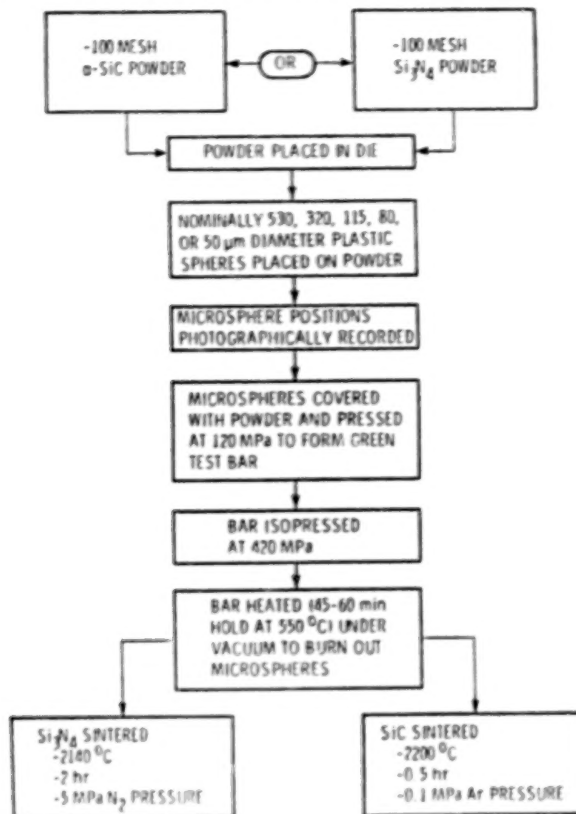
NONDESTRUCTIVE EVALUATION OF STRUCTURAL CERAMICS*

Alex Vary
Lewis Research Center
Cleveland, Ohio 44135

A review is presented on research for nondestructive evaluation (NDE) of structural ceramics for heat engine applications. Microfocus radiography and scanning laser acoustic microscopy are the NDE techniques highlighted in this review. The techniques were applied to research samples of sintered silicon nitride and silicon carbide in the form of modulus-of-rupture (MOR) bars. The strengths and limitations of the aforementioned techniques are given in terms of probability of detection for voids in green and sintered MOR bars. Voids for this purpose were introduced by seeding green ceramic bars and characterizing each void in terms of its size, shape, location, and nature before and after sintering. The effects of material density, microstructure, surface finish, thickness, void depth, and size characteristics on detectability are summarized. The review presented here is based on the work of Stanley Klima, Don Roth, George Baaklini, William Sanders, and James Kiser of Lewis Research Center, Cleveland, Ohio.

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FABRICATION OF MODULUS-OF-RUPTURE (MOR) BARS CONTAINING SEEDED INTERNAL VOIDS



EXPERIMENTAL/ANALYTICAL

- SPECIALLY PREPARED MODULUS-OF-RUPTURE TYPE BARS WERE SYSTEMATICALLY SEEDED WITH CRITICAL SIZE VOIDS
- VOIDS RESULTED AFTER THE STYRENE DIVINYLBENZENE MICROSPHERES WERE DECOMPOSED IN THE GREEN CERAMICS AT 550° C
- POD STATISTICS WERE DETERMINED USING THE CUMULATIVE PROBABILITY FORMULA

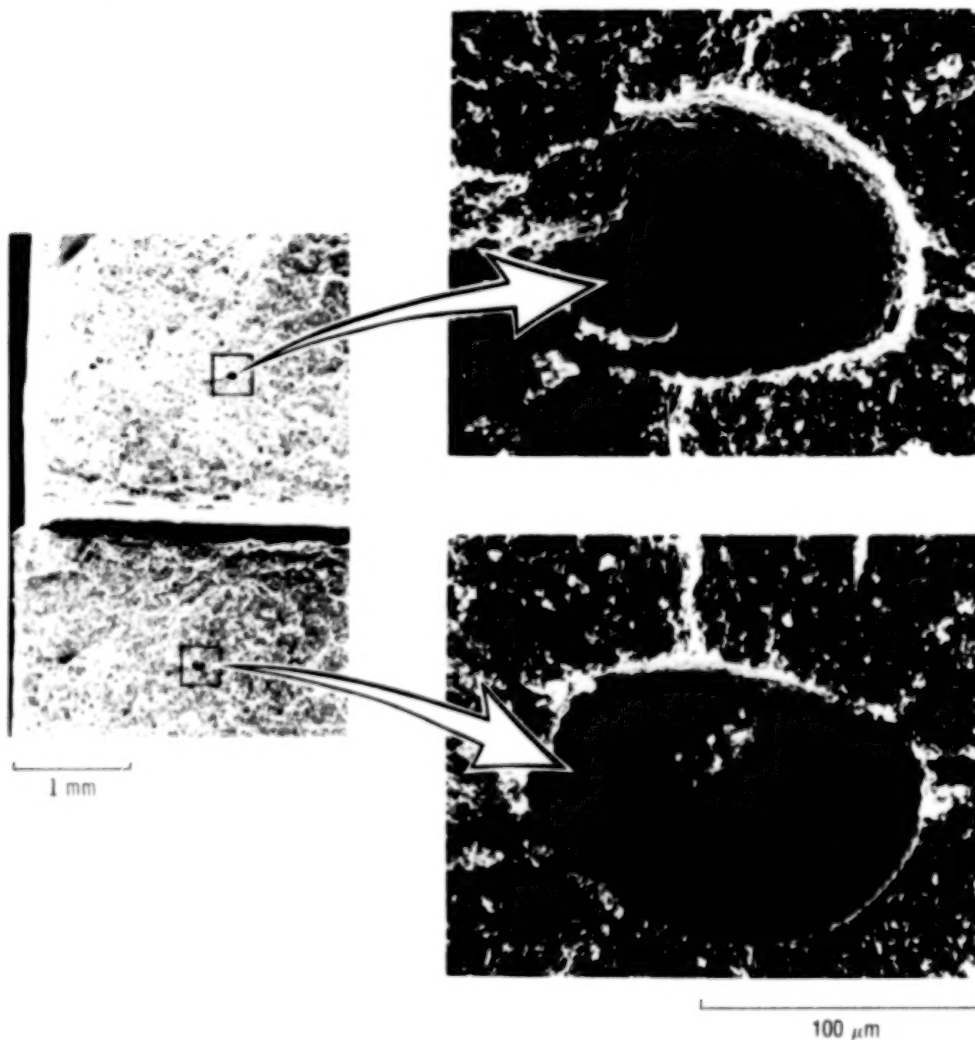
$$1 - G = \sum_{X=S}^N \frac{N!}{X! (N-X)!} P_L^X (1 - P_L)^{N-X}$$

WHERE P_L IS THE LOWER-BOUND PROBABILITY OF DETECTION, G IS THE CONFIDENCE LEVEL, N IS THE NUMBER OF VOIDS SEEDED, AND S IS THE NUMBER OF VOID DETECTED

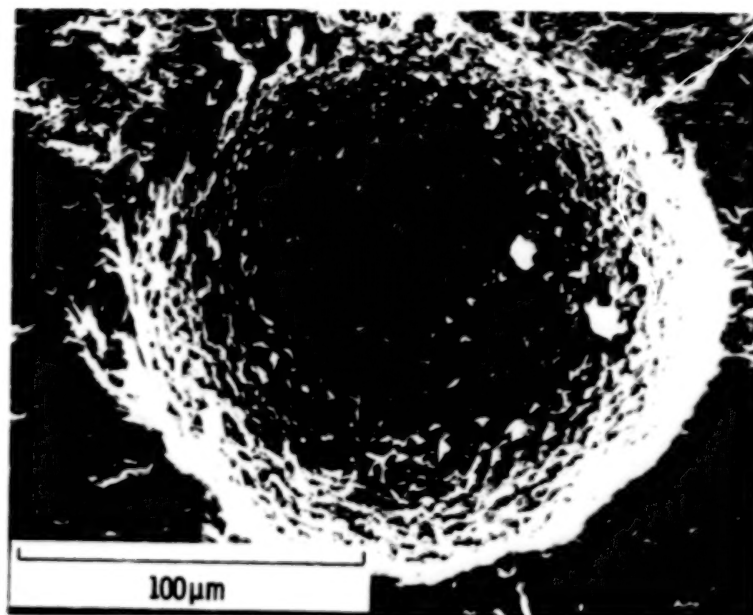
DIMENSIONAL CHARACTERISTICS OF RESULTING INTERNAL VOIDS IN SINTERED MATERIALS

MATERIALS	SPECIMEN THICKNESS RANGE,	SPHERE diam, μm	NUMBER OF SPHERES SEEDED	RESULTING VOID DIMENSION			
				VOID DEPTH, μm		VOID DIAMETER, μm	
				MEAN	STANDARD DEVIATION	MEAN	STANDARD DEVIATION
Si_3N_4	2-7	80	69	20	4	25	6
		115	39	37	5	68	5
		200	31	133	17	135	8
		321	28	233	16	267	18
		528	21	307	14	386	15
SiC	2-7	50	50	32	3	58	3
		80	47	59	6	100	8
		115	68	77	10	131	8
		200	19	165	29	194	11
		321	39	297	19	307	15
		528	43	477	47	505	28

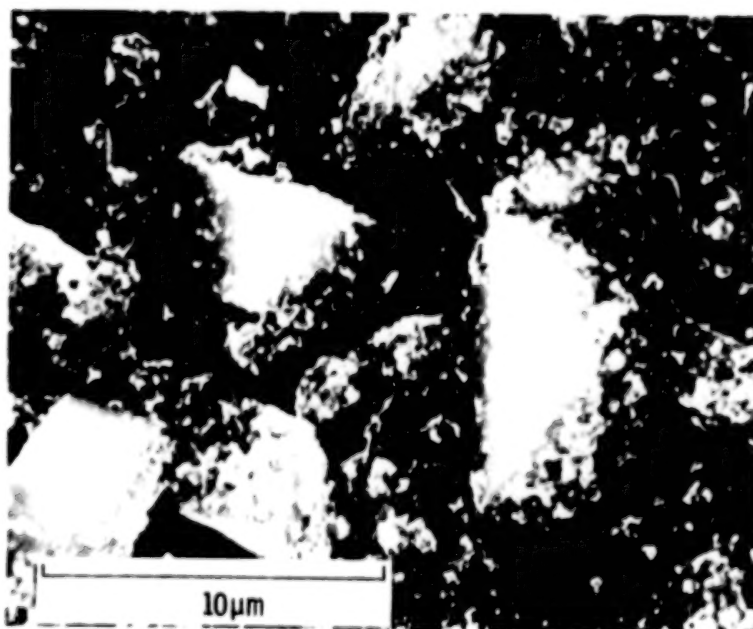
SCANNING ELECTRON FRACTOGRAPHS SHOWING TYPICAL INTERNAL VOIDS IN GREEN SIC BARS



SCANNING ELECTRON MICROGRAPHS OF A TYPICAL VOID IN SINTERED SiC BARS



AS EXPOSED TO SURFACE

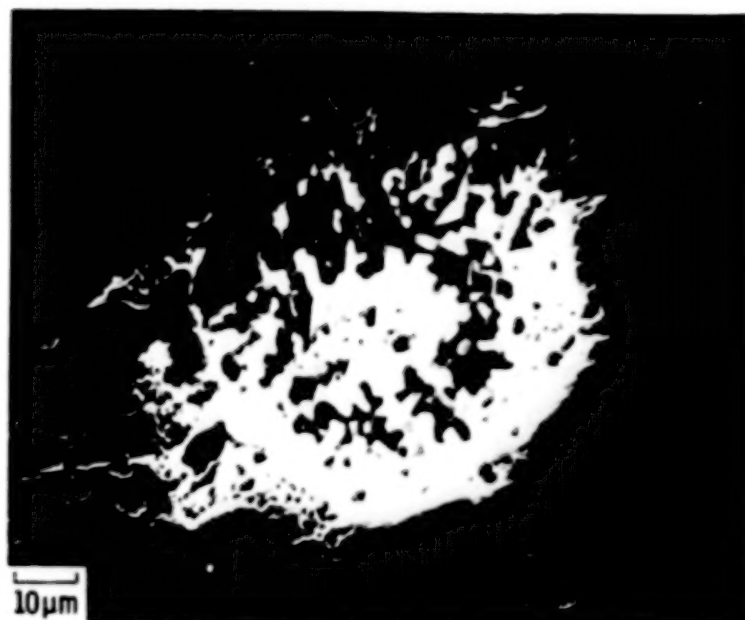


TEXTURE OF THE CAVITY-WALL-SURFACE

ORIGINAL PAGE IS
OF POOR QUALITY

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SCANNING ELECTRON MICROGRAPHS OF TYPE A INTERNAL VOIDS IN SINTERED Si_3N_4



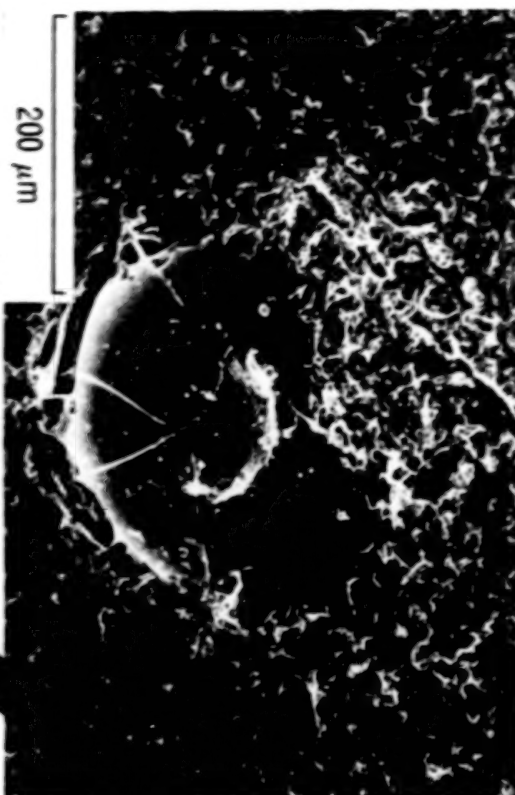
AS EXPOSED TO SURFACE



CLUSTERS OF GRAINS PROJECTING FROM THE CAVITY WALLS

SCANNING ELECTRON MICROGRAPHS OF TYPE B INTERNAL VOIDS IN SINTERED Si_3N_4

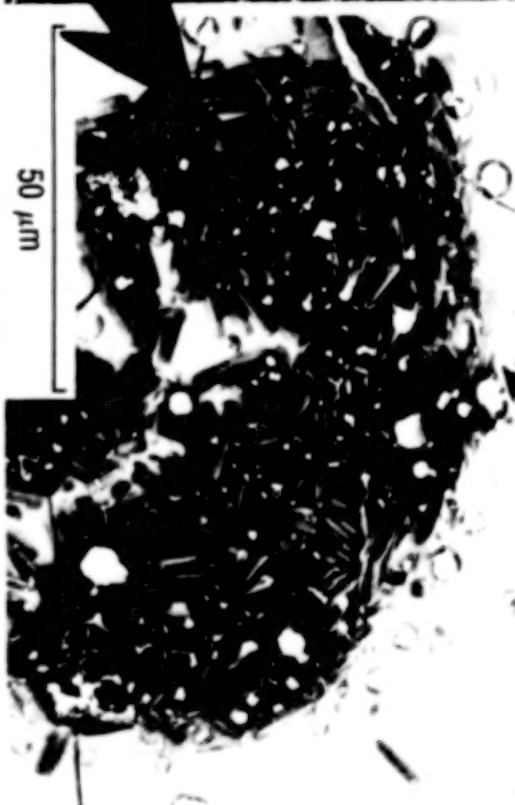
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AS EXPOSED TO SURFACE



BACKSCATTERED ELECTRON IMAGE

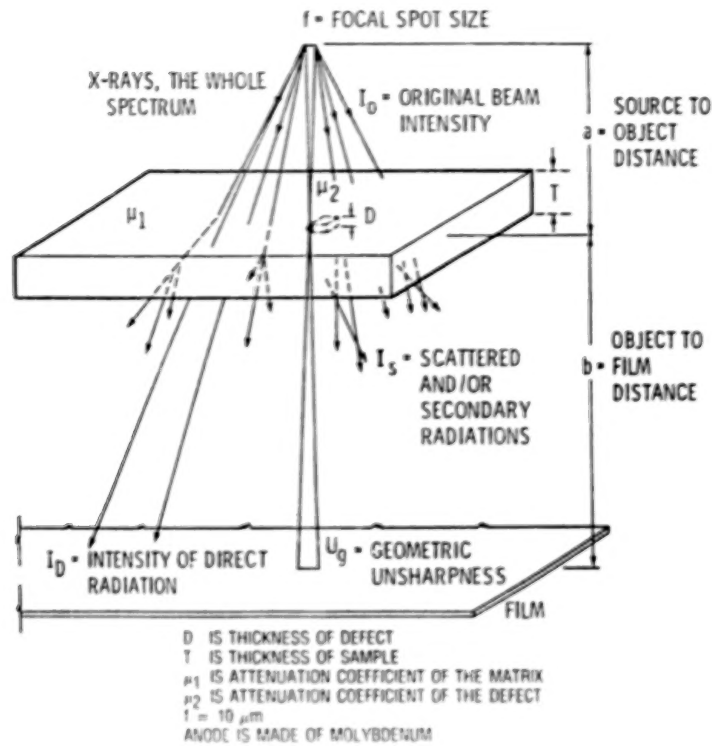


BACKSCATTERED ELECTRON IMAGE AT MODERATE
MAGNIFICATION



BACKSCATTERED ELECTRON IMAGE AT HIGH MAGNIFICATION

A SCHEMATIC CONFIGURATION OF MICROFOCUS PROJECTION RADIOGRAPHY



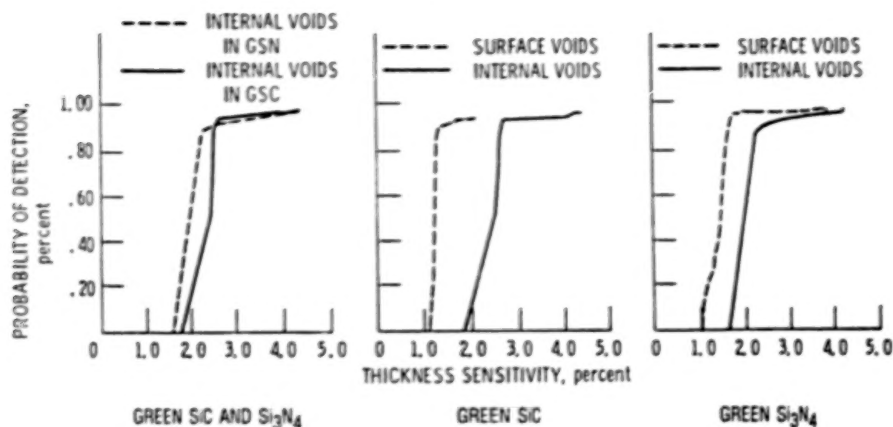
MICROFOCUS RADIOGRAPHY

SUMMARY OF POD STATISTICS FOR INTERNAL AND SURFACE VOIDS IN GREEN AND SINTERED SiC AND Si₃N₄

MATERIALS		OPTIMUM SENSITIVITY AT 90/95 POD/CL* (GIVEN AS PERCENT OF SAMPLE THICKNESS)	
		INTERNAL VOIDS	SURFACE VOIDS
SiC	GREEN	2.6	1.4
	SINTERED	1.5	1.7
Si ₃ N ₄	GREEN	2.4	1.5
	SINTERED	0.6	1.5

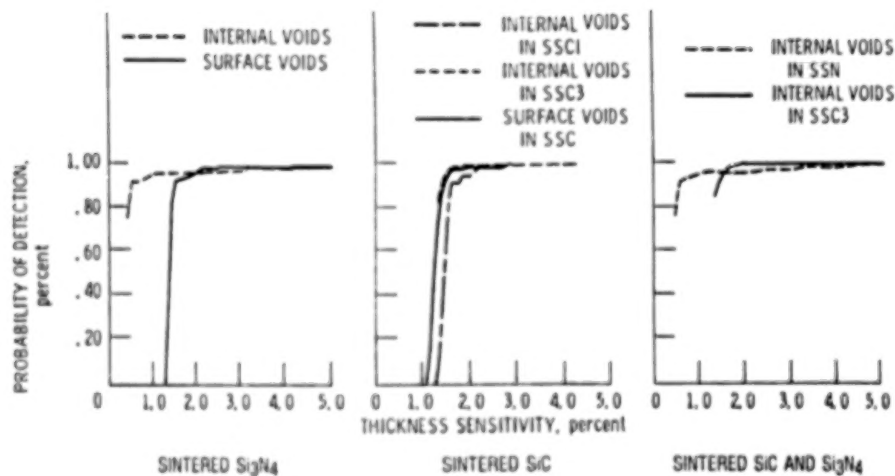
- 90/95 POD/CL (PROBABILITY OF DETECTION/CONFIDENCE LEVEL)
MEANS THAT THERE IS A 5% PROBABILITY THAT THE 90% IS
AN OVERESTIMATE OF THE PROBABILITY OF DETECTION

LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN GREEN ISOPRESSED SIC (GSC) AND Si_3N_4 (GSN) BARS



- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY % = 100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/(THICKNESS OF SPECIMEN IN SAME DIRECTION)

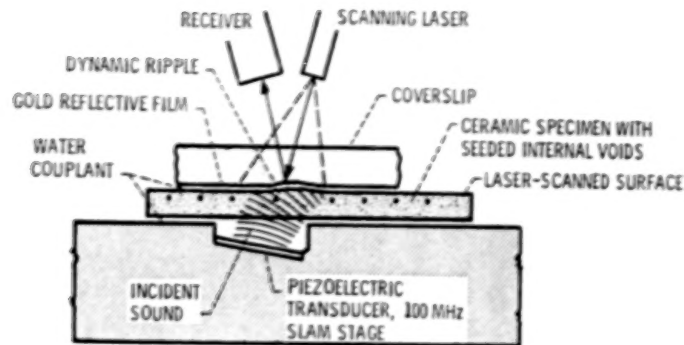
LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN SINTERED SIC (SSC) AND Si_3N_4 (SSN) BARS



- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY % = 100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/(THICKNESS OF SPECIMEN IN SAME DIRECTION)

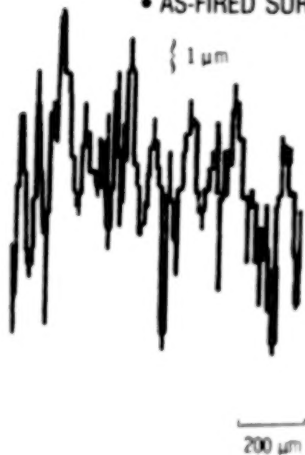
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**SCHEMATIC ILLUSTRATION OF THE SCANNING
LASER ACOUSTIC MICROSCOPE**

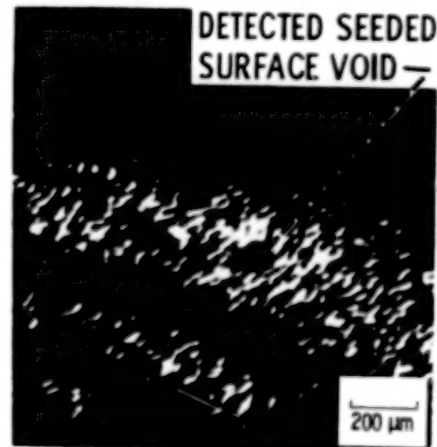


**EFFECT OF SPECIMEN SURFACE CONDITION ON
SLAM IMAGE CLARITY**

- AS-FIRED SURFACE PRODUCES A HIGHER BACKGROUND NOISE LEVEL



AS-FIRED SURFACE PROFILE.

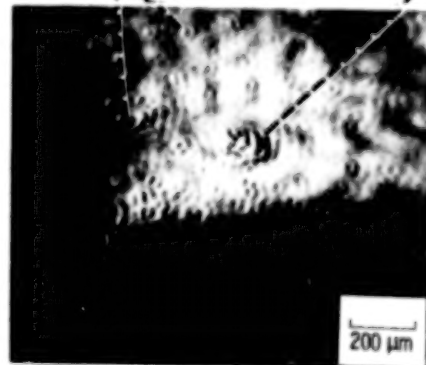


ACOUSTIC MICROGRAPH OF AS-FIRED SPECIMEN.



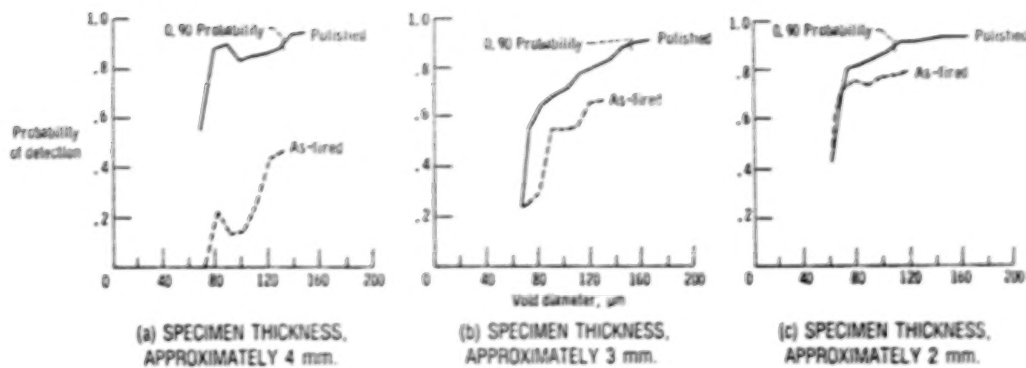
HAND-POLISHED SURFACE PROFILE.

NATURALLY OCCURRING
IMPERFECTIONS



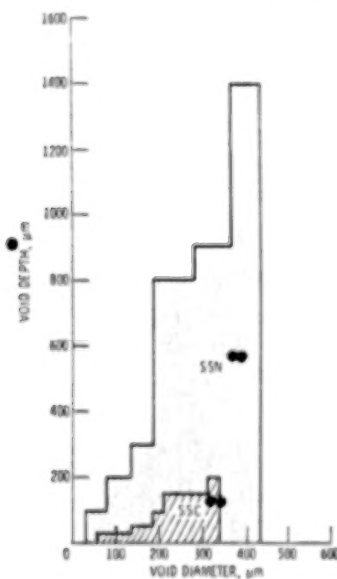
ACOUSTIC MICROGRAPH OF HAND-POLISHED SPECIMEN.

EFFECT OF SURFACE FINISH AND SPECIMEN THICKNESS ON DETECTION OF VOIDS IN SSN



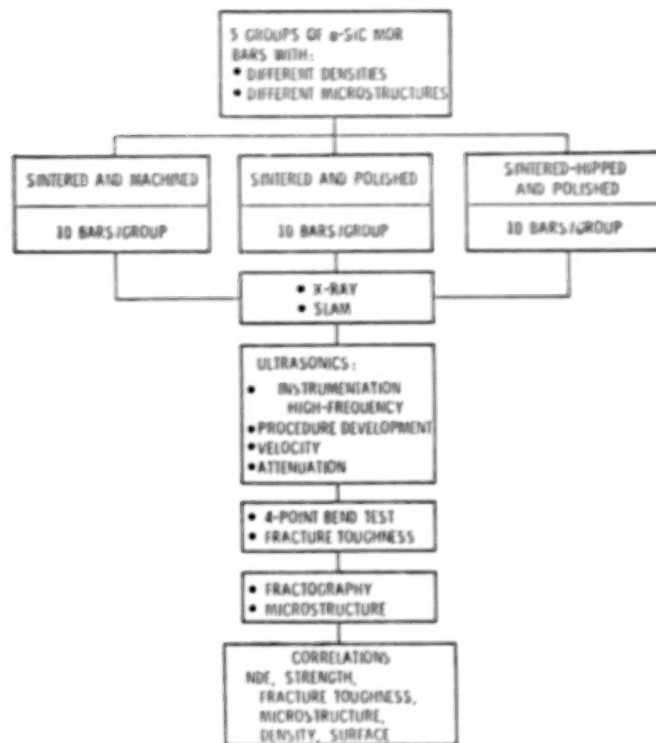
EFFECT OF VOID DIAMETER, VOID DEPTH, AND MATRIX MATERIAL ON PROBABILITY OF DETECTION BY SLAM

90% PROBABILITY OF DETECTION AT 95% CONFIDENCE LIMIT



- DEPTH BELOW WHICH A VOID WITH A SPECIFIED DIAMETER CANNOT BE DETECTED AT $\text{POD/CL} = 90/95$
- DETECTABILITY OF SMALLER, DEEPER VOIDS IN SSN MAY BE ATTRIBUTABLE TO FINER GRAINS AND GREATER DENSITY (SSN AT $> 99\%$ VS SSC AT $\sim 97\%$ THEORETICAL DENSITY)

NDE FOR CHARACTERIZING CERAMIC MICROSTRUCTURES



ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si_3N_4

		SUB-SURFACE PORE	SURFACE PORE	SEAM	SUB-SURFACE AGGLOMERATE	COLUMNAR GRAIN	SURFACE DEFECT	METALLIC INCLUSION
R. T. FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	192 ^a	56	44	28	25	17	13
	PERCENT OF TOTAL	100	29	23	14	13	9	7
1200 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	90 ^a	23	19	9	7	14	0
	PERCENT OF TOTAL	100	26	21	10	8	15	0
1370 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	127 ^a	30	15	25	3	32	0
	PERCENT OF TOTAL	100	24	12	20	2	25	0

^aNUMBER EXCLUDES 111, 47, AND 41 BARS FOR R.T., 1200 °C, AND 1370 °C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.

SUMMARY

SCANNING LASER ACOUSTIC MICROSCOPY

VOID DETECTABILITY WAS AFFECTED BY MATERIAL, MICROSTRUCTURE, SURFACE FINISH, SPECIMEN THICKNESS, VOID DEPTH, AND VOID SIZE.

- VOIDS WERE MORE EASILY DETECTED IN SINTERED SILICON NITRIDE (SSN) THAN IN SINTERED SILICON CARBIDE (SSC). SSN GRAIN SIZE WAS AN ORDER OF MAGNITUDE SMALLER THAN IN SSC.
- VOID DETECTABILITY WAS SIGNIFICANTLY IMPROVED BY SURFACE GRINDING. IN SPECIMENS WITH AS-FIRED SURFACES, 0.90/0.95 POD/CL WAS NOT ACHIEVED FOR ANY VOID SIZE UP TO 160 μm .
- LITTLE OR NO THICKNESS EFFECT ON DETECTABILITY WAS OBSERVED IN SPECIMENS WITH GROUND SURFACES. IN SPECIMENS WITH AS-FIRED SURFACES, DETECTABILITY IMPROVED WITH DECREASING THICKNESS.

MICROFOCUS X-RAY RADIOGRAPHY

DETECTABILITY OF VOIDS WAS AFFECTED BY PHOTON ENERGY LEVEL, MATERIAL COMPOSITION IN THE VICINITY OF THE VOID, DENSITY VARIATIONS, SAMPLE THICKNESS AND VOID SIZE.

- LOW PHOTON ENERGY LEVELS (≤ 20 KeV) PRODUCED BETTER RADIOGRAPHIC FILM CONTRAST AND HENCE BETTER VOID DETECTABILITY THAN HIGHER ENERGY LEVELS.
- YITTRIUM MIGRATING TO THE WALLS OF SEEDED VOIDS AIDED DETECTION OF SOME BUT NOT ALL VOIDS IN SSN. YITTRIA SINTERING AID WAS THE SOURCE.
- DETECTABILITY OF VOIDS DID NOT APPEAR TO BE ADVERSELY AFFECTED BY AS-FIRED SURFACES RELATIVE TO DIAMOND GROUND SURFACES.
- THE THRESHOLD LEVEL OF DETECTION OF VOIDS WAS 1.5 PERCENT OF SPECIMEN THICKNESS OR 50 μm , WHICHEVER IS GREATER, WHEN THE 0.90/0.95 POD/CL CRITERIA WAS APPLIED.

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Cleveland, Ohio 44135

The application of fracture mechanics to the design of ceramic structures will require the precise measurement of crack growth and fracture resistance of these materials over their entire range of anticipated service temperatures and standardized test methods for making such measurements. The development of a standard test for measuring the plane strain fracture toughness is the initial objective of our ceramics fracture mechanics program.

Current fracture tests make use of a variety of specimen types (single-edge-notched bend, double torsion, double cantilever bend, and surface flawed specimens) having either blunt notches produced by saw cutting, or cracks produced by wedge loading, indenting, or local thermal shock. Specimens with blunt notches can overestimate the fracture toughness. Precracked specimens are difficult to prepare in a reproducible manner, and the initial crack front often cannot be seen on the fracture surface after testing, which makes it impossible to measure the initial crack length. These difficulties can be circumvented by using a specimen containing a chevron notch in which a crack originates at the tip of the triangular ligament during the early stage of specimen loading. Specimens with a chevron notch were first used by Nakayama in fracture studies (ref. 1). Later they were used by Tattersall and Tappin for fracture surface energy measurements (ref. 2) and more recently, by Barker for plane strain fracture toughness measurements (ref. 3). The essential features of the chevron-notch specimen are that (1) a sharp natural crack is produced during the early stage of loading (no precracking is required) and (2) the load passes through a maximum at a constant material-independent crack length-to-width ratio for a specific specimen geometry (no post-test crack length measurement is required). For materials with flat crack growth resistance curves, the plane strain fracture toughness is proportional to the maximum test load and a function of the specimen geometry and elastic compliance.

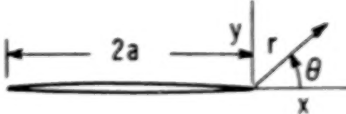
Stress intensity factor coefficients have been determined for three varieties of chevron-notch specimens, and fracture toughness measurements have been made on silicon nitride, silicon carbide, and aluminum oxide to assess the performance of each specimen variety. It has been determined that silicon nitride and silicon carbide have flat crack growth resistance curves, but aluminum oxide does not. Additionally, batch-to-batch differences have been noticed for the aluminum oxide. Experiments are continuing to explain the rising crack growth resistance and batch-to-batch variations for the aluminum oxide.

REFERENCES

1. Nakayama, J.: Direct Measurement of Fracture Energies of Brittle Heterogeneous Materials. J. Am. Ceram. Soc., vol. 48, no. 11, 1965, pp. 583-587.
2. Tattersall, H.G.; and Tappin, G.: The Work of Fracture and Its Measurement in Metals, Ceramics and other Materials. J. Mater. Sci., vol. 1, no. 3, 1966, pp. 296-301.
3. Barker, L.M.: A Simplified Method for Measuring Plane Strain Fracture Toughness. Eng. Fracture Mech., vol. 9, no. 2, 1977, pp. 361-369.

PLANE STRAIN ELASTIC STRESS FIELD IN VICINITY OF CRACK TIP

$$\sigma_x = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left(1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) + \dots$$

$$\sigma_y = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left(1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) + \dots$$


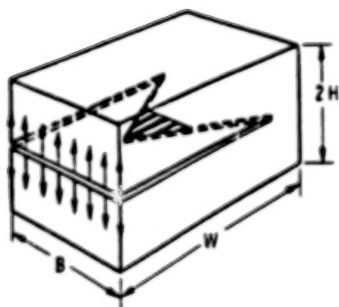
$$\tau_{xy} = \frac{K_I}{(2\pi r)^{1/2}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} + \dots$$

$$\sigma_z = \nu(\sigma_x + \sigma_y); \tau_{xz} = \tau_{yz} = 0$$

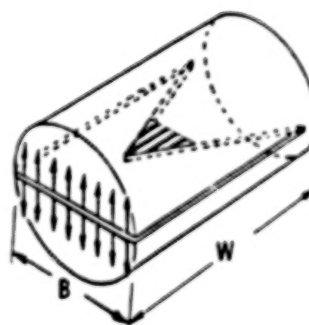
K_I IS THE "STRESS INTENSITY FACTOR"

K_{Ic} IS THE "FRACTURE TOUGHNESS"

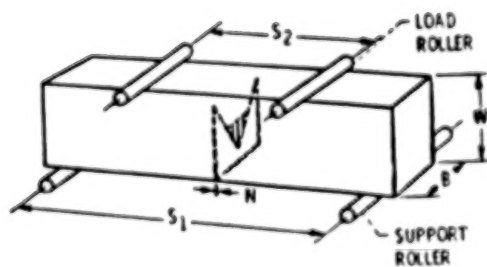
CHEVRON-NOTCH SPECIMENS



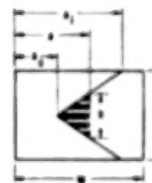
SHORT BAR



SHORT ROD



FOUR-POINT BEND



CRACK PLANE
SECTION

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THEORETICAL BASIS FOR CHEVRON-NOTCH SPECIMEN K_{Ic} MEASUREMENT

AVAILABLE ENERGY FOR EXTENSION OF CRACK BY Δa :

$$\Delta U = \frac{P^2}{2W} \cdot \frac{dC_{tr}}{da} \cdot \Delta a$$

NECESSARY ENERGY FOR EXTENSION OF CRACK BY Δa :

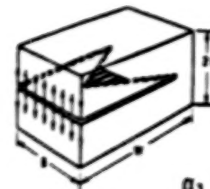
$$\Delta \bar{W} = G_{Ic} \cdot b \cdot \Delta a = \frac{K_{Ic}^2}{E} \cdot b \cdot \Delta a$$

DURING CRACK EXTENSION $\Delta U = \Delta \bar{W}$, $\therefore$ D:

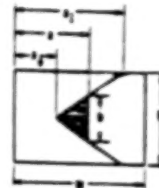
$$K_{Ic} = P \left[\frac{E}{2bW} \frac{dC_{tr}}{da} \right]^{1/2}$$

$$\text{AND SINCE } b = B \left[\frac{a - a_0}{a_1 - a_0} \right] = B \left[\frac{a - a_0}{a_1 - a_0} \right]$$

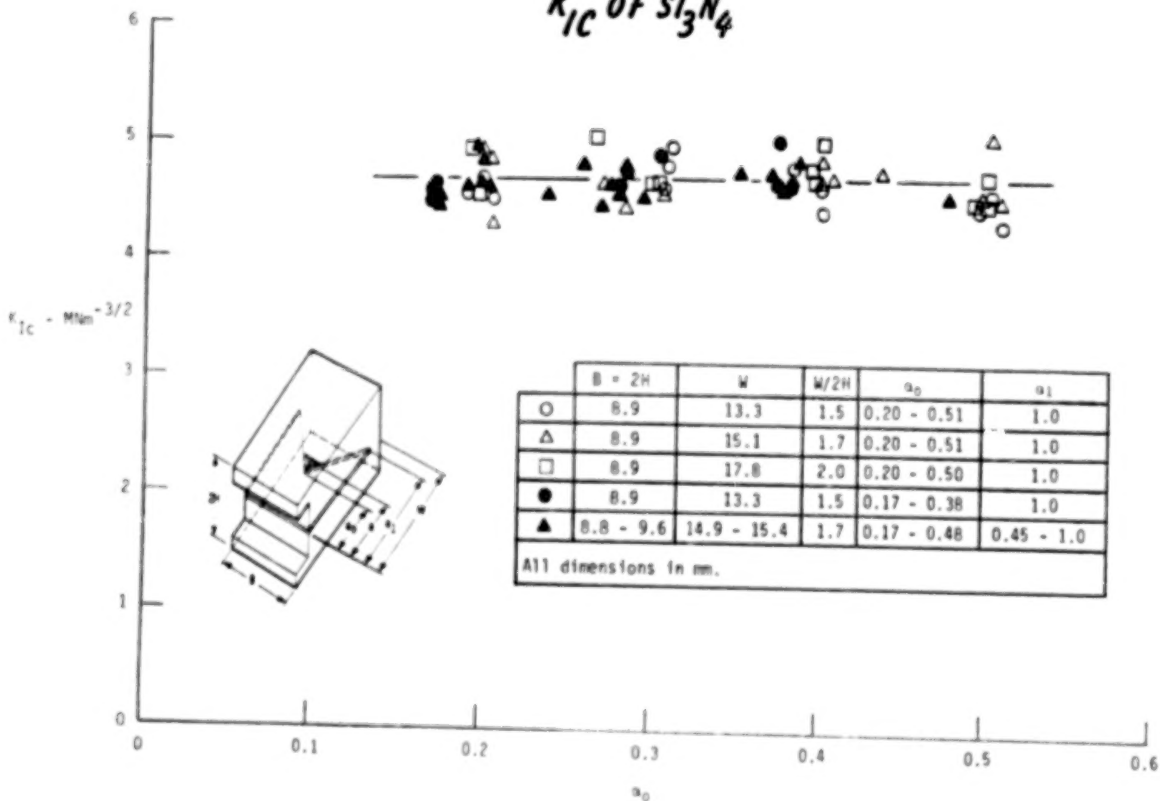
$$K_{Ic} = P \left[\frac{E}{2WB \left(\frac{a - a_0}{a_1 - a_0} \right)} \frac{dC_{tr}}{da} \right]^{1/2} = \frac{P}{B/W} \left[\frac{EB}{2} \frac{dC_{tr}}{da} \left(\frac{a_1 - a_0}{a - a_0} \right) \right]^{1/2} = \frac{P}{B/W} \gamma^*$$



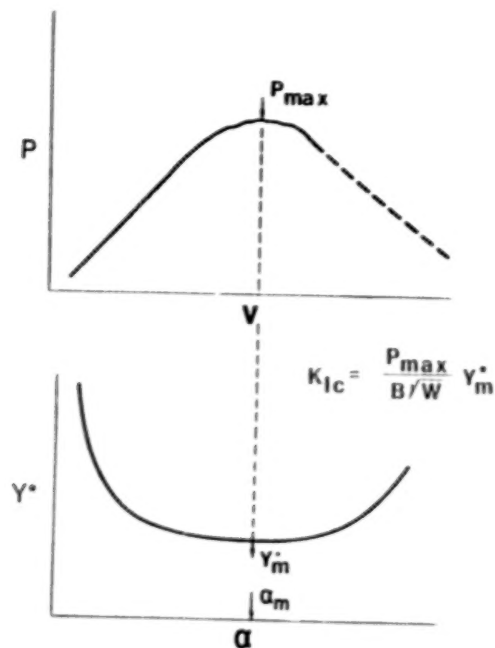
$$\begin{aligned} a_1 &= a_1/W \\ a &= a/W \\ a_0 &= a_0/W \end{aligned}$$



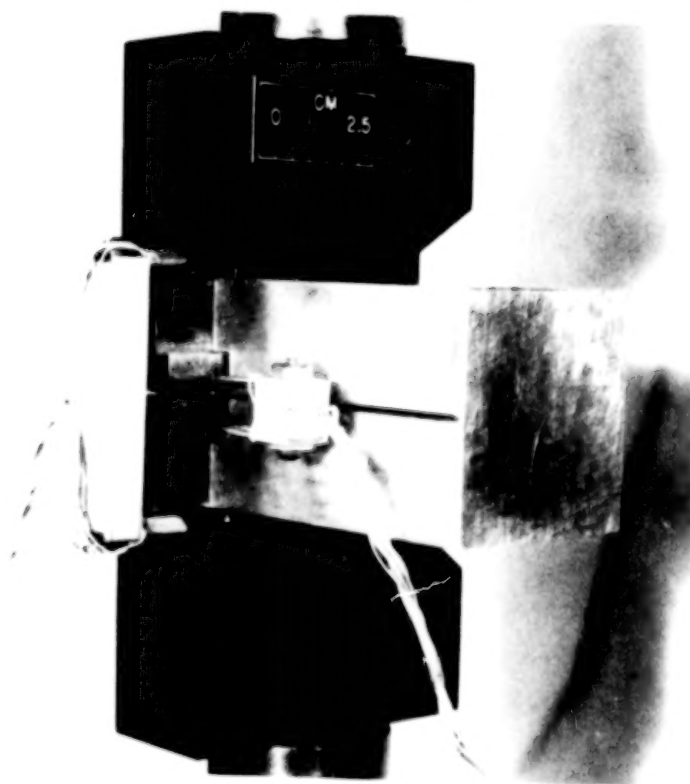
K_{Ic} OF Si_3N_4



CHEVRON-NOTCH SPECIMEN K_{Ic} FROM P_{max} AND Y_m^*

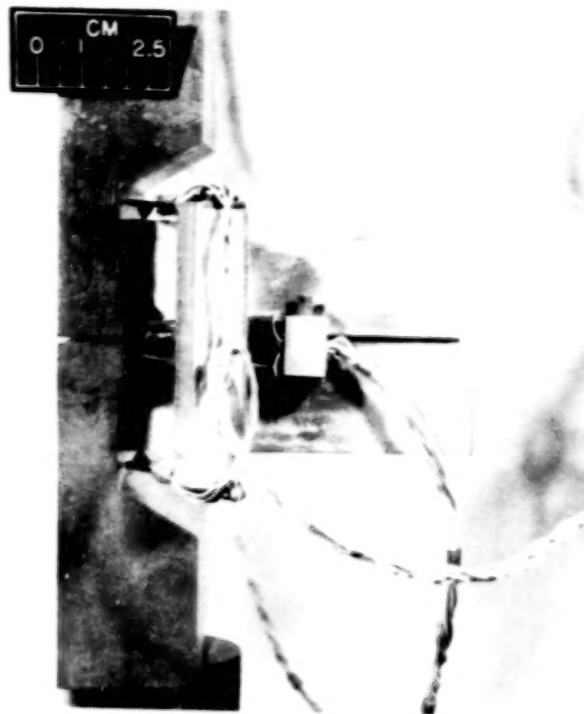


CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

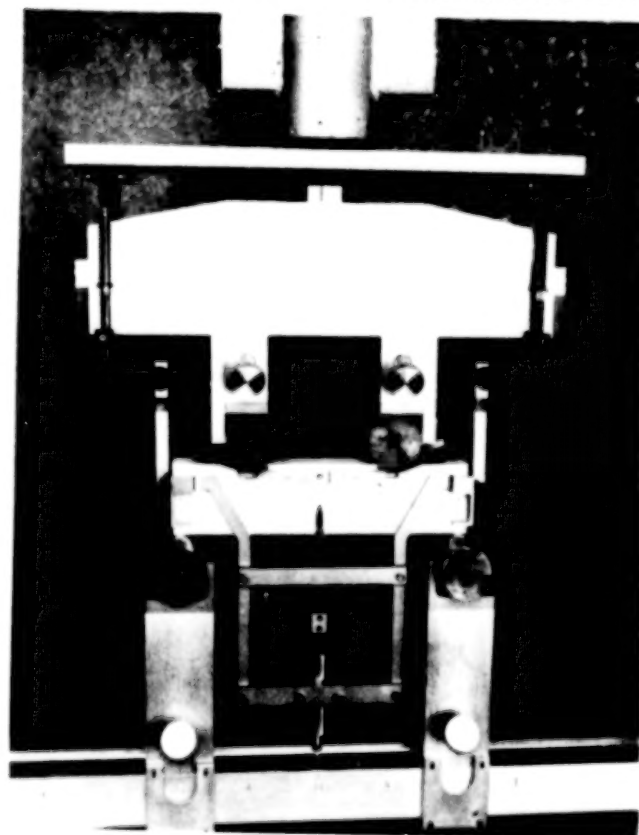


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CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP



CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

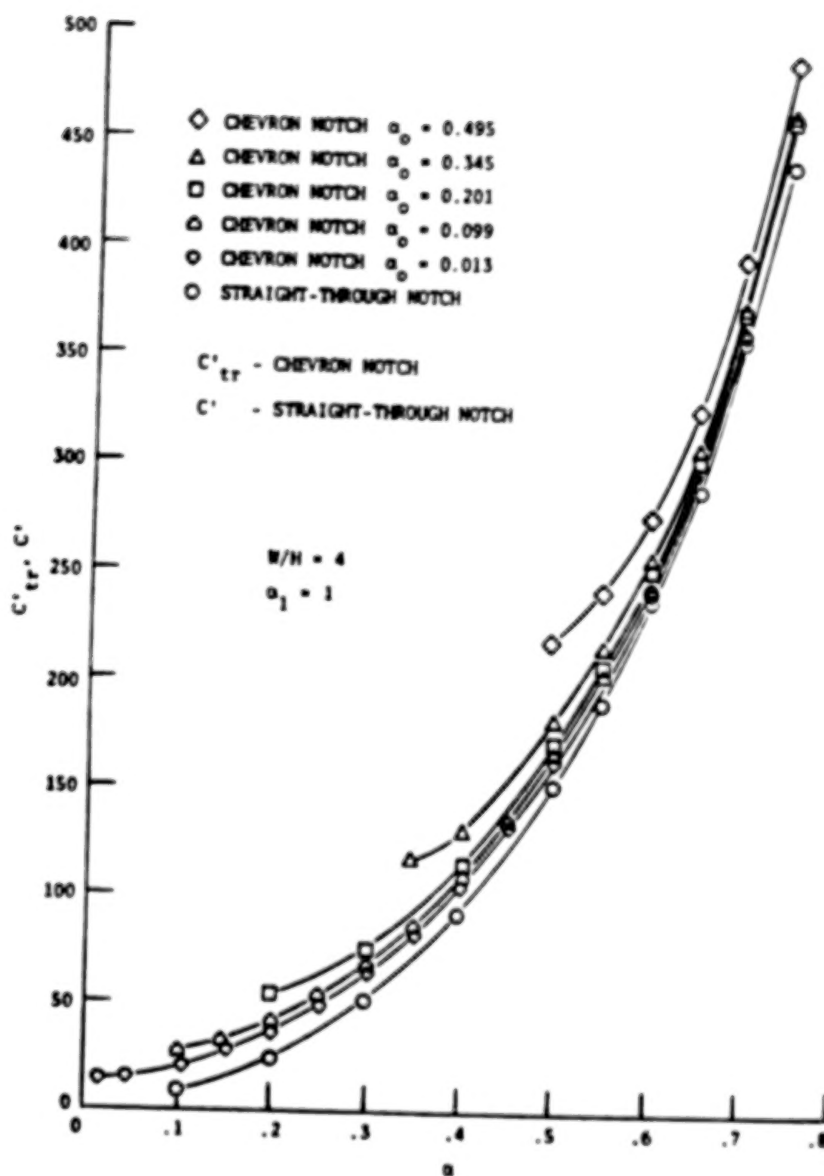


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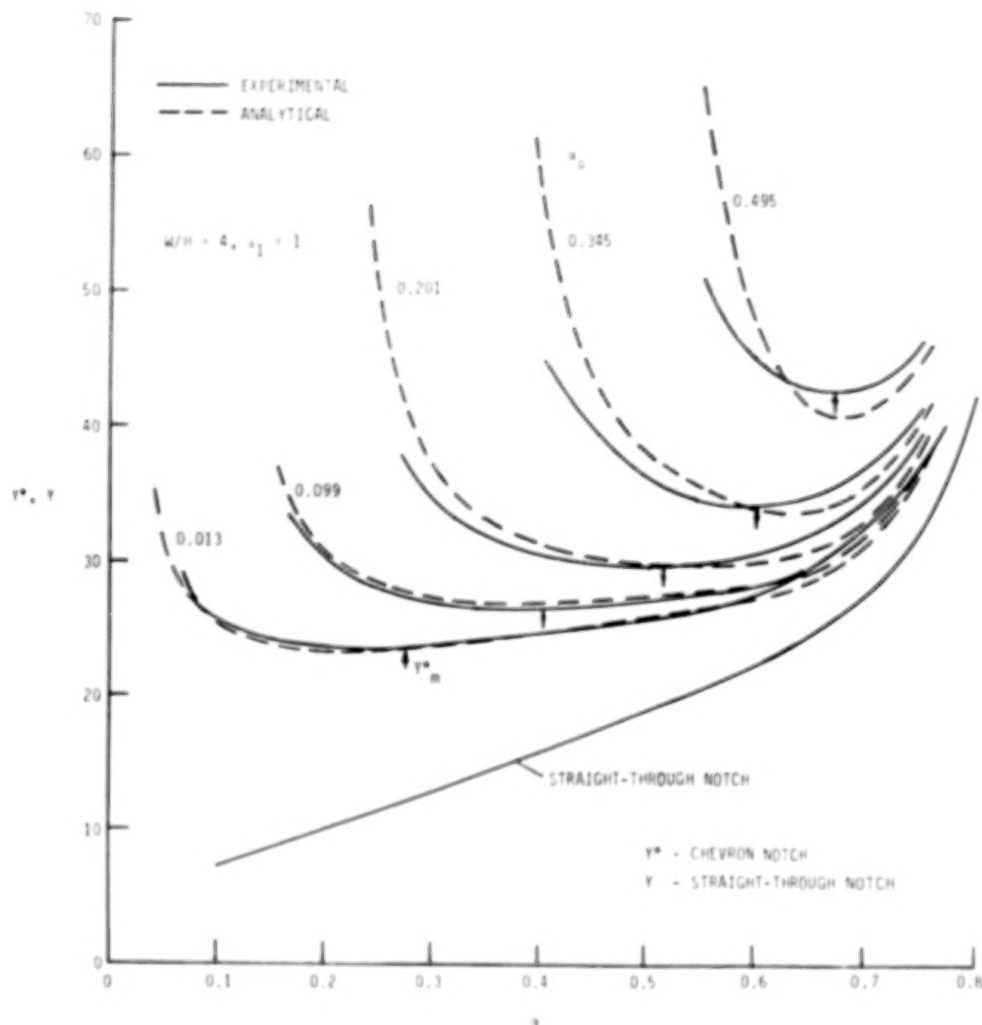
CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

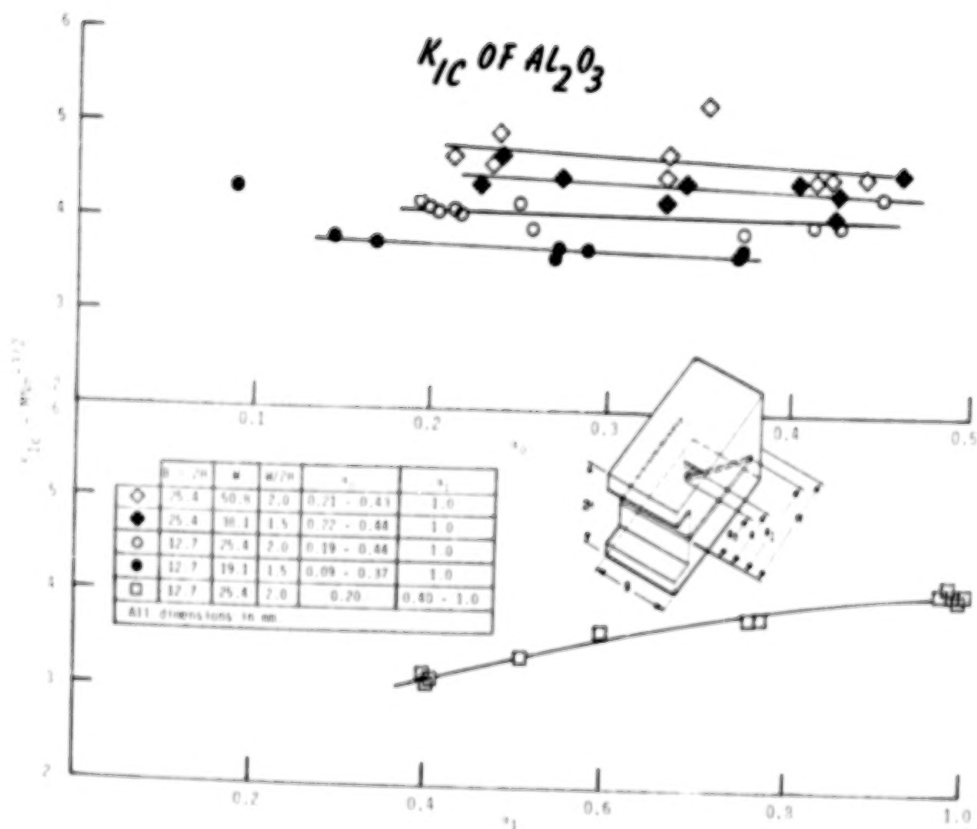
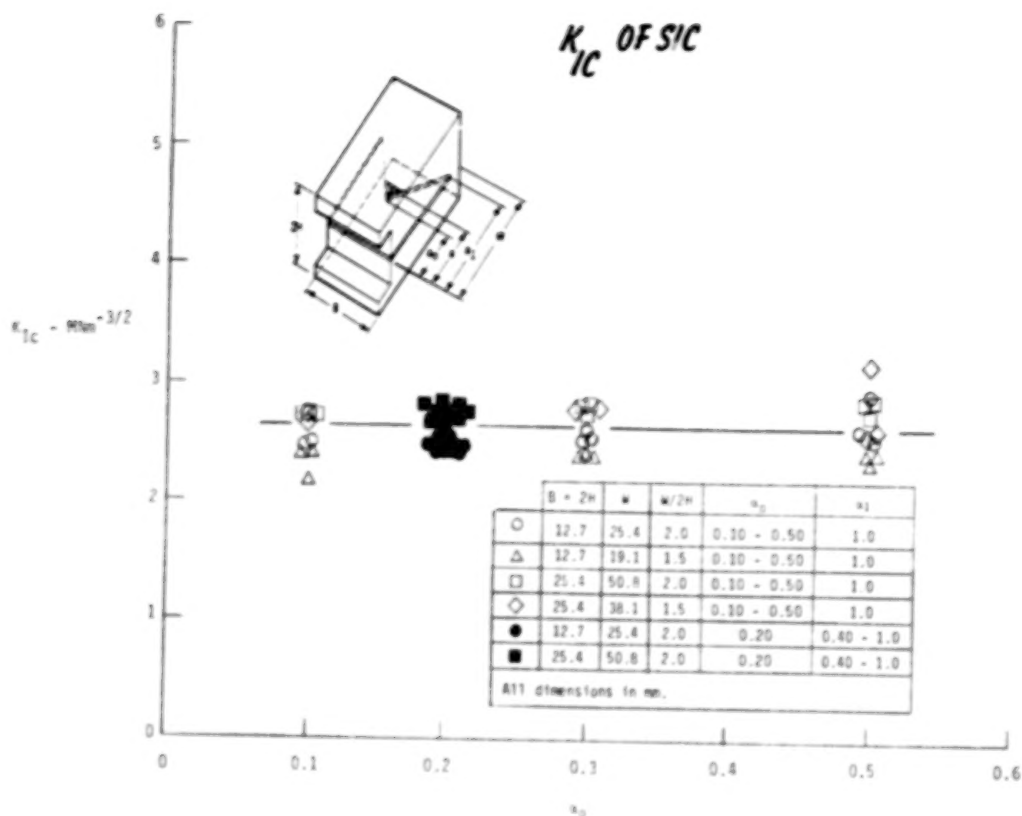


CHEVRON-NOTCH SHORT BAR SPECIMEN DIMENSIONLESS COMPLIANCE



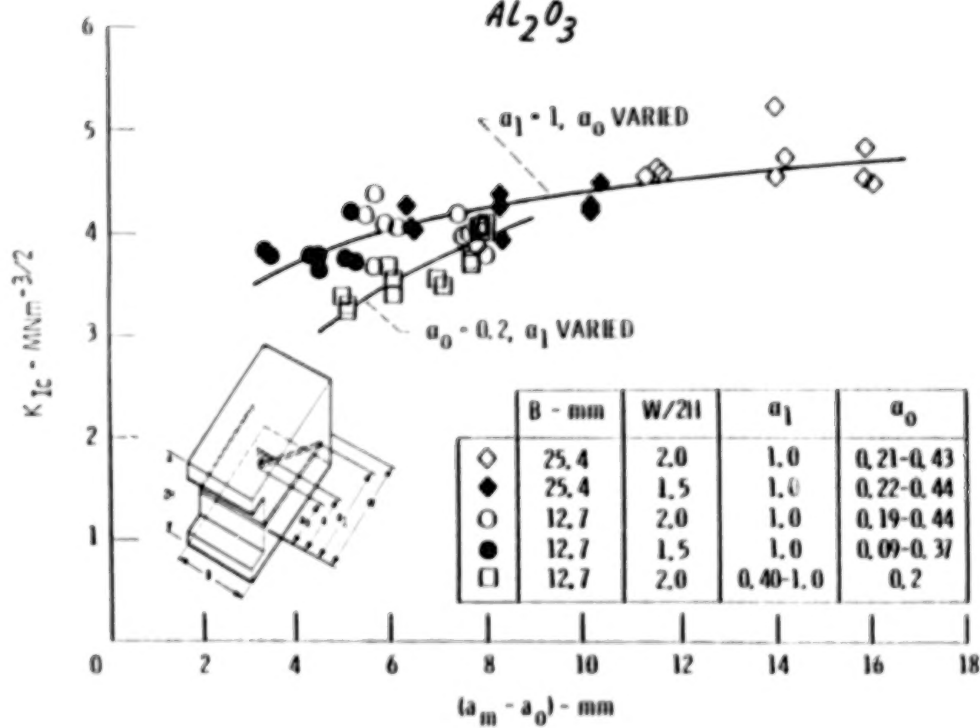
CHEVRON-NOTCH SHORT BAR SPECIMEN STRESS INTENSITY FACTOR COEFFICIENTS





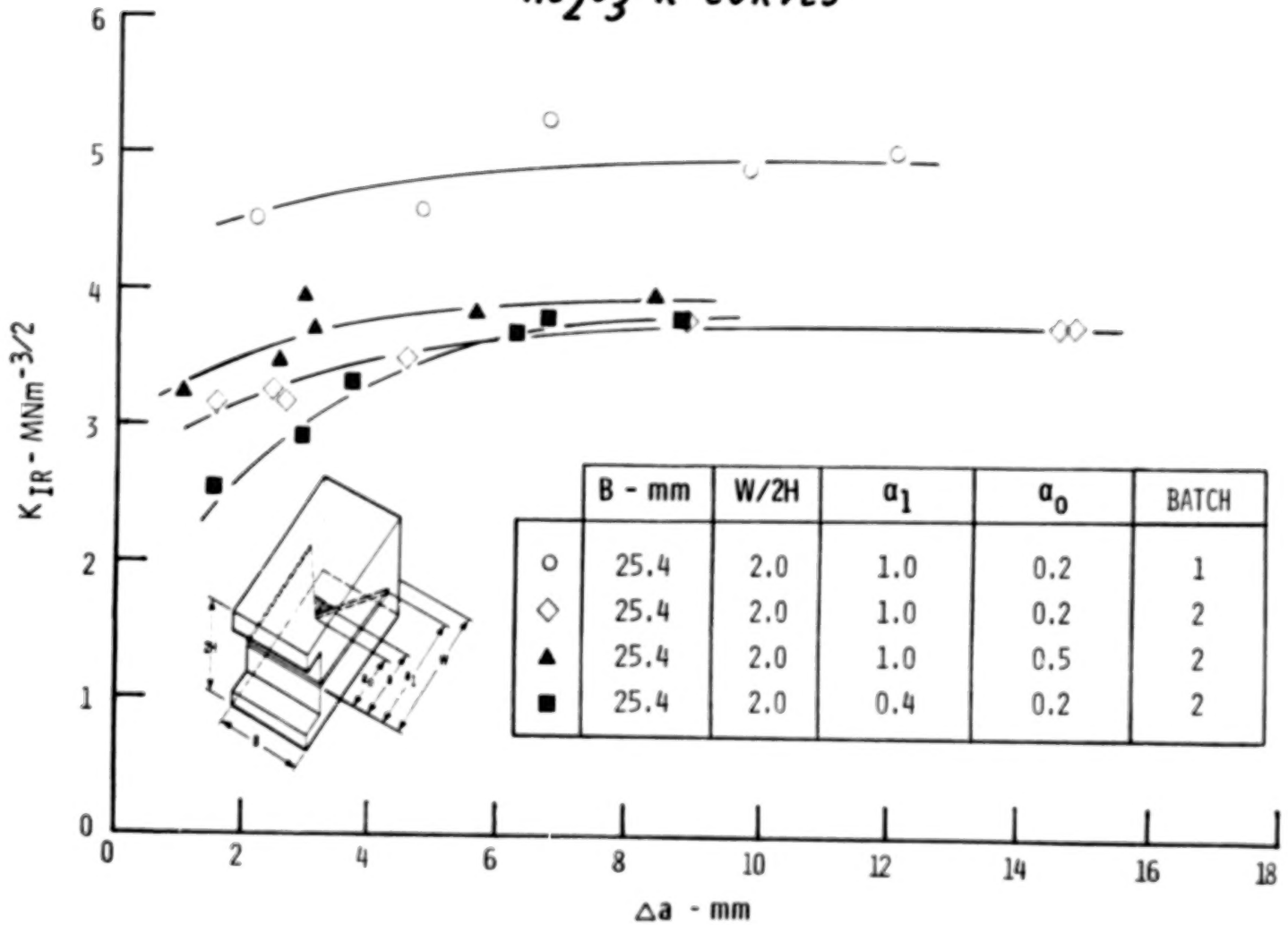
VARIATION IN K_{IC} WITH CRACK EXTENSION TO P_{MAX}

Al_2O_3



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Al_2O_3 R-CURVES



N88-23878

P-4

STRUCTURAL CERAMICS RESEARCH

J.I. Mueller, R.J.H. Bollard, and R.C. Bradt
University of Washington
Seattle, Washington

OUTLINE

CERAMIC RESEARCH AT U. OF W.

BRITTLE MATERIALS DESIGN PROGRAM

NASA PROGRAM RESEARCH AT U. OF W.

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STRUCTURAL CERAMIC RESEARCH at U. of W.

AKSAY, I.	MSE	powder processing, sintering
BERG, J.	CHE	colloidal studies
BJORKSTAM, J.	EE	NDE/NDT
BOLLARD, R.J.H.	AA	evaluation, design
BRADT, R.	MSE	mechanical properties
DASH, G.	PHY	thermal conditions
EMERY, A.	ME	thermal stresser
FISCHBACH, D.	MSE	fiber composite, carbon
HARTZ, B.	CE	design
KIKUCHI, R.	MSE	theoretical modeling
KOBAYASHI, A.	ME	mechanical prop., dynamic fracture
LIN, K.	AA	elast. mechanical comp.
MILLER, A.	MSE	processing, environ. effects
RAMULU, M.	ME	dynamic fracture, machining
RAO, Y.	MSE	nitridation Si
REED, D.	CE	design
SARIKAYA, M.	MSE	characterization
SCOTT, W.	MSE	oxidation
STOEBE, T.	MSE	nitridation, defects
TAGGART, R.	ME	design
TAYA, M.	ME	comp. mechanics
WHITTEMORE, O.	MSE	processing

BRITTLE MATERIALS DESIGN PROGRAM (COURSE)

BRITTLE MATERIALS

PROCESSING of CERAMICS

ELASTICITY

MECHANICAL CHARACTERIZATION

MICROSTRUCTURE /MECHANICAL PROPERTIES

ENGINEERING PROPERTIES of CERAMICS

STRENGTH and FAILURE THEORIES

NDE/NDT

DESIGN of COMPONENTS

LABORATORY (PP) COMPONENT MANUFACTURE

CURRENT NASA RESEARCH PROGRAM AT UW

I. PROCESSING AND CHARACTERIZATION

STOEBE - Lattice Defects in Si_3N_4

RAO - Nitridation of Si

AKSAY - Powder Consolidation by Injection
Molding

SCOTT - Oxidation Resistance of Si_3N_4

II. MECHANICAL PROPERTIES

MILLER - Environmental Effects on Si_3N_4 , SiC

EMERY - Thermal Fracture

KOBAYASHI - Impact, Erosion, Dynamic Fracture

BOLLARD - Evaluation of Mechanical Tests

BRADT/REED - Micromechanical Stresses

PROPOSED 86/87 CERAMIC/COMPOSITES RESEARCH TOPICS

AKSAY - POWDER PROCESSING

RAO - NITRIDATION

MILLER - COMPOSITE NITRIDATION

BERG - COLLOIDAL PROCESSING OF
COMPOSITES

EMERY - THERMAL PROPERTIES

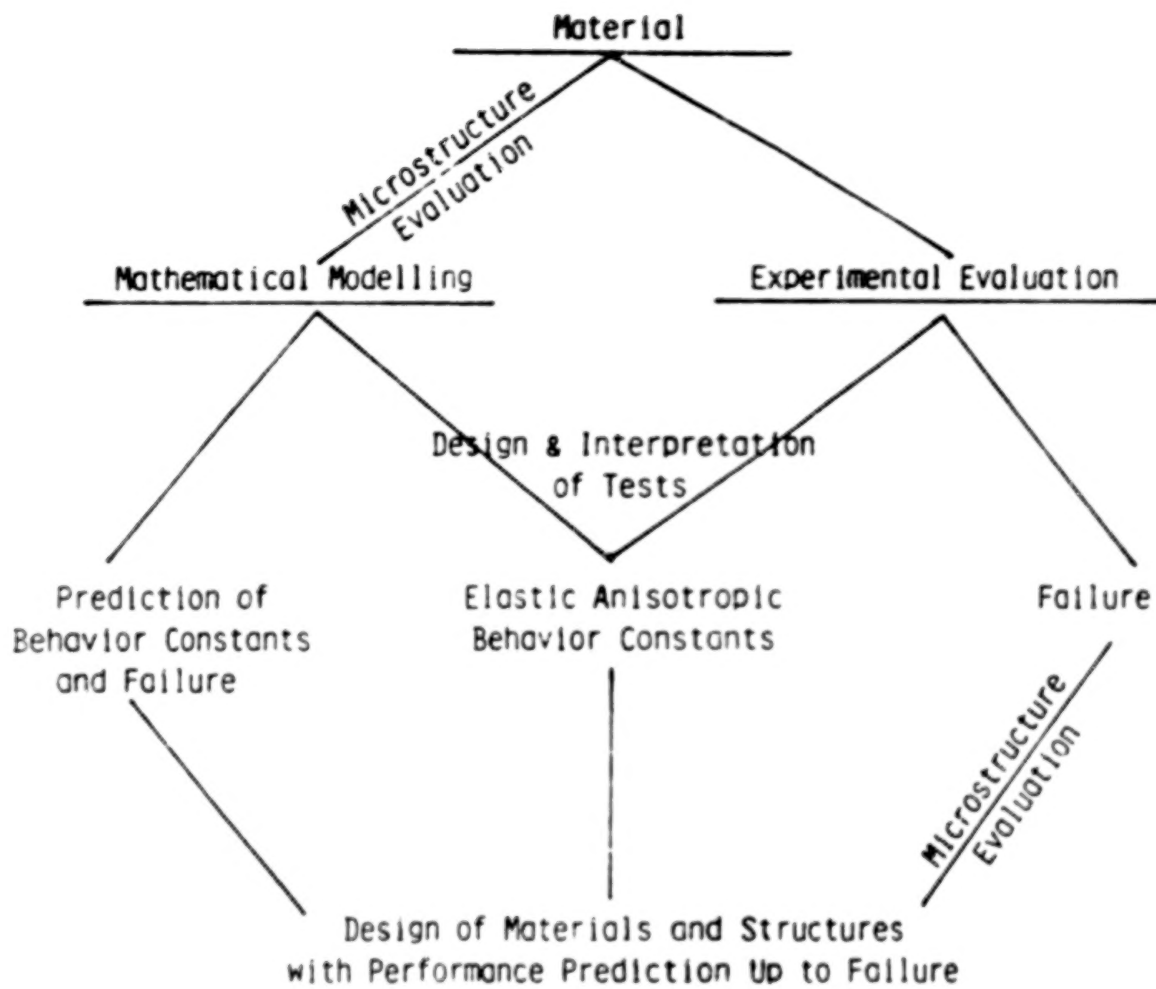
KOBAYASHI - DYNAMIC MECHANICAL
PROPERTIES

TAYA - THERMAL CYCLING FATIGUE

BRADT/REED - ANISOTROPIC RESIDUAL
STRESSES

BOLLARD - MECHANICAL CHARACTERIZATION

COMPOSITE CHARACTERIZATION



1-7
N88-23879 P26

IMPROVED SILICON CARBIDE FOR ADVANCED HEAT ENGINES*

Thomas J. Whalen and J.A. Mangels
Ford Motor Company F03534

This report describes work performed in the first year of the program conducted for NASA to develop silicon carbide materials of high strength and to form components of complex shape and high reliability. The approach has been to adapt a beta-SiC powder and binder system to the injection molding process and to develop procedures and process parameters capable of providing a sintered silicon carbide material with improved properties.

The initial effort has been to characterize the baseline precursor materials (beta silicon carbide powder and boron and carbon sintering aids), develop mixing and injection molding procedures for fabricating test bars, and characterize the properties of the sintered materials. Parallel studies of various mixing, dewaxing, and sintering procedures have been performed in order to distinguish process routes for improving material properties.

A total of 276 MOR bars of the baseline material have been molded, and 122 bars have been fully processed to a sinter density of approximately 95 percent. The material has a mean MOR room temperature strength of 43.3 ksi (299 mPa), a Weibull characteristic strength of 45.8 ksi (315 mPa) and a Weibull modulus of 8.0. Mean values of the MOR strengths at 1000 °C, 1200 °C and 1400 °C are 41.4 ksi, 43.2 ksi and 47.2 ksi, respectively. Strength controlling flaws in this material were found to consist of regions of high porosity and were attributed to agglomerates originating in the initial mixing procedures.

New fluid mixing techniques have been developed which significantly reduce flaw size and improve the strength of the material. Initial MOR tests indicate the strength of the fluid-mixed material exceeds the baseline property by more than 33 percent.

Plans for the development of the fluid-mixing process to reduce flaw size and increase density and the optimization of sinter-body microstructure to increase toughness of the silicon carbide materials will be reviewed.

Contributions to this program were made by the following.

Ford Motor Company: R. Govila, B.N. Juterbock, J.A. Mangels, V. Mindroiu, L.R. Reatherford, S.S. Shinozaki, W. Trela, T.J. Whalen, R.M. Williams, and W.L. Winterbottom

NASA: S. Levine and N. Shaw

*Work performed under NASA Contract No. NAS3-24384

FIRST YEAR REVIEW

T. J. Whalen

J. A. Mangels

May 21, 1986

OBJECTIVE :

Develop High Strength, High Reliability Silicon Carbide Parts Having Complex Shapes by a Method Adaptable to Mass Production on an Economically Sound Basis.

APPROACH :

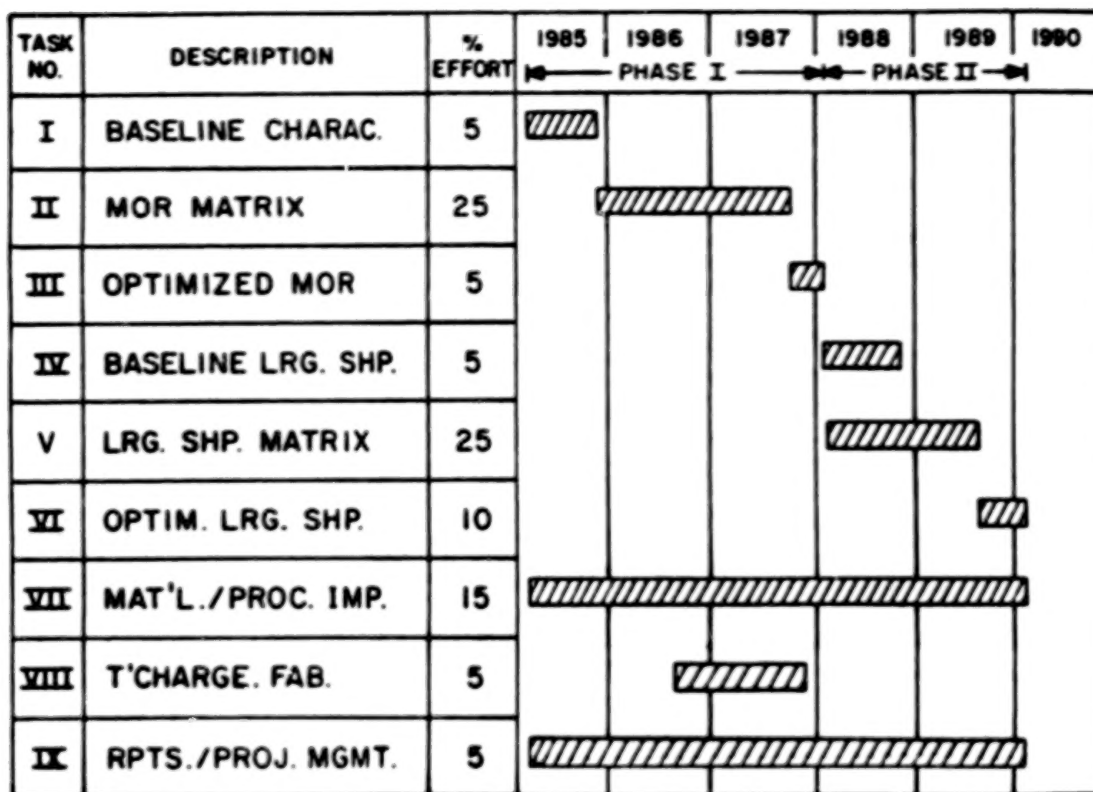
Adapt Powder and Binder System to Injection Molding Process and Develop Procedures and Optimize Process Parameters Leading to a Sintered Silicon Carbide Material with Improved Properties.

BENEFITS :

Silicon Carbide Parts for Advanced Gas Turbines and Other Heat Engines Would Permit Higher Temperature Operation with Resulting Fuel Efficiencies.

START / FINISH :

February, 1985 to February, 1988



Timing Chart

OUTLINE

TASK I

T. J. WHALEN

- * BASELINE POWDERS CHARACTERIZATION
- * BASELINE COMPOSITION SELECTION
- * BASELINE RESULTS

TASK VII AND PLANS

J. A. MANGELS

- * PROCESSING AND COMPOSITION IMPROVEMENTS
- * PLANNING

TASK I

BASELINE CHARACTERIZATION

POWDERS

CHEMICAL ANALYSIS - BASELINE MATERIAL

ELEMENT	UF-SiC	BORON	CARBON
C	30.4 ^a	0.36	98.6
O	0.85	1.71	1.12
Al	0.046	0.040	
Fe	0.043	0.17	0.005
Ca	0.019	0.046	
Mg	0.015	0.55	
Ti	0.005	0.047	
Zr	0.005		
S			0.25

^a Weight Percent

B.E.T. SURFACE AREA

As Received Powders for Baseline Bars

Ibiden UF	Lot 0166	SiC	21.5 M ² /g
Starck	Lot S-3506	B	12.1 M ² /g
Monsanto	Lot TL-246	C	53.1 M ² /g

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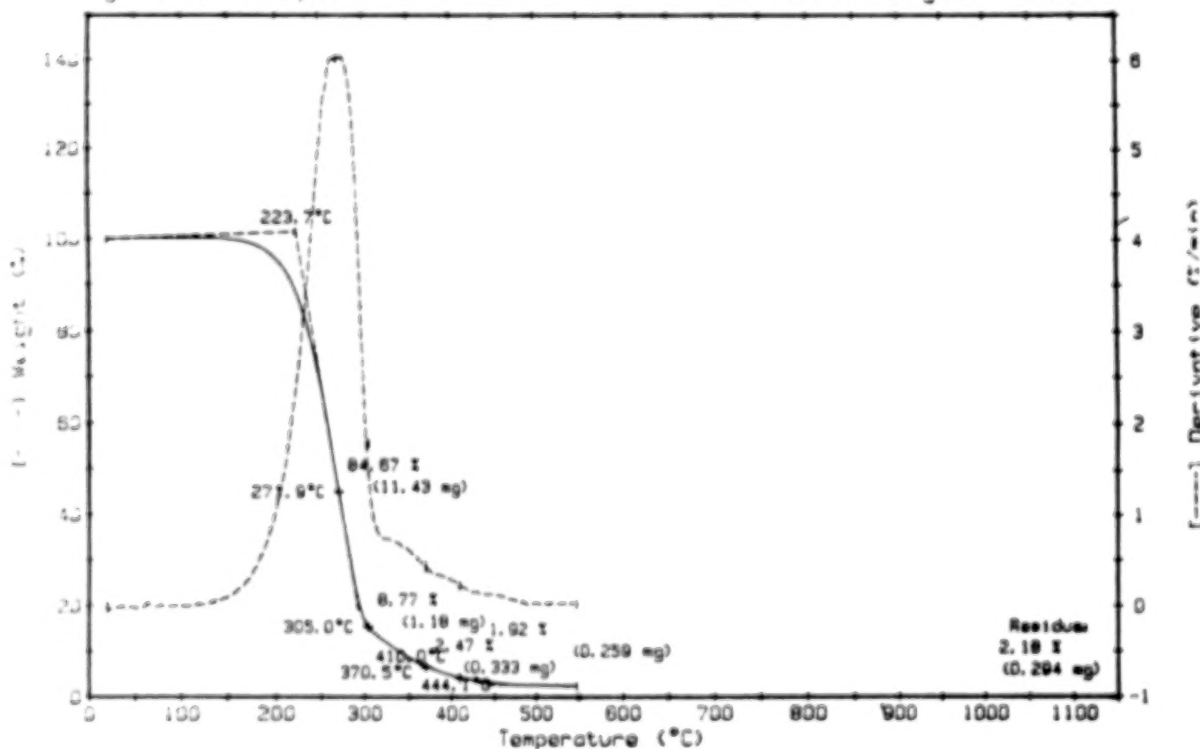
PARTICLE DIAMETER, SPECIFIC GRAVITY, PACK DENSITY,
AND POLYPHASE ANALYSIS OF SiC POWDER FOR BASELINE BARS

Particle Diameter	Volume Dist.	Frequency Dist
<u>UF Lot 0166</u>		
Median	1.05	0.61
Mode	1.16	0.64
Geometric Mean	1.04	0.59
Arithmetic Mean	1.18	0.65
Specific Gravity		
	3.161 gm/cm ³	
Pack Density		
	0.787 gm/cm ³	
<u>X-ray Polyphase Analysis</u>		
3C Phase	84.0 %	
Disordered Phase	16.0 %	

Sample: RMW-PARAFFIN CARBURA LG₁
Size: 13.50 mg
Rate: 50.0 MIN 100ML/MIN ARG
Program: TGA Analysis V2.0

TGA

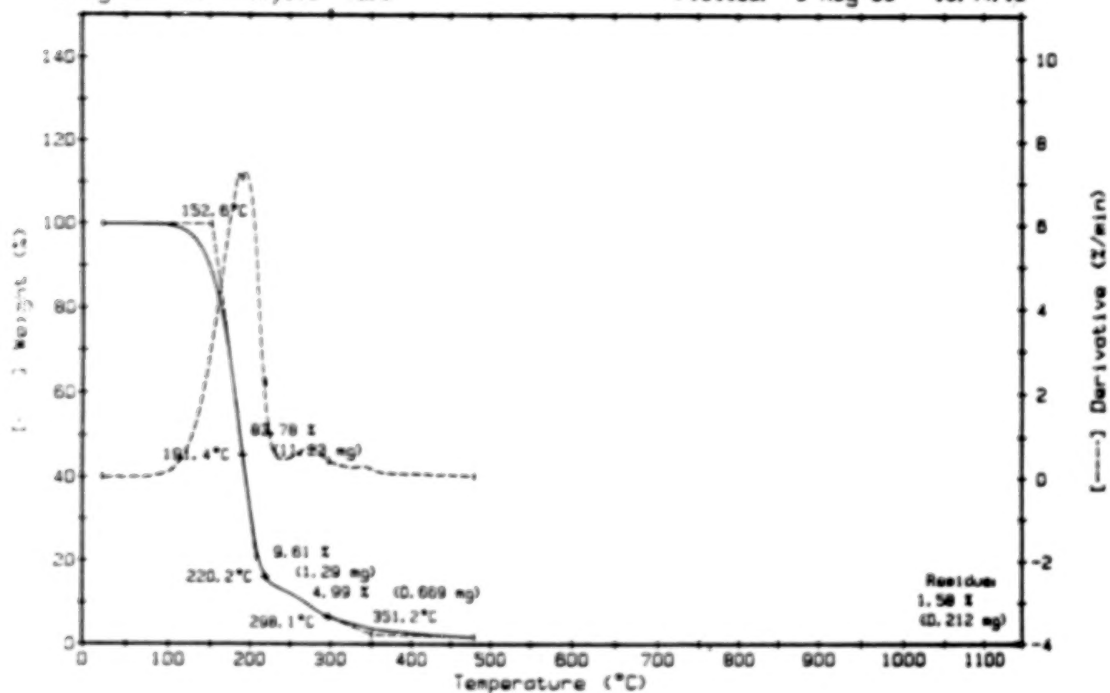
Date: 26-Aug-85 Time: 8:11:08
File: TGA.01 TGA.8AUG.1985
Operator: L. SKEWES
Plotted: 26-Aug-85 10:56:43



Sample: RM-1-PARAFFIN LOW CARNUBA
 Size: 13.41 mg
 Rate: 50/MIN 8mm Hg
 Program: TGA Analysis V2.0

TGA

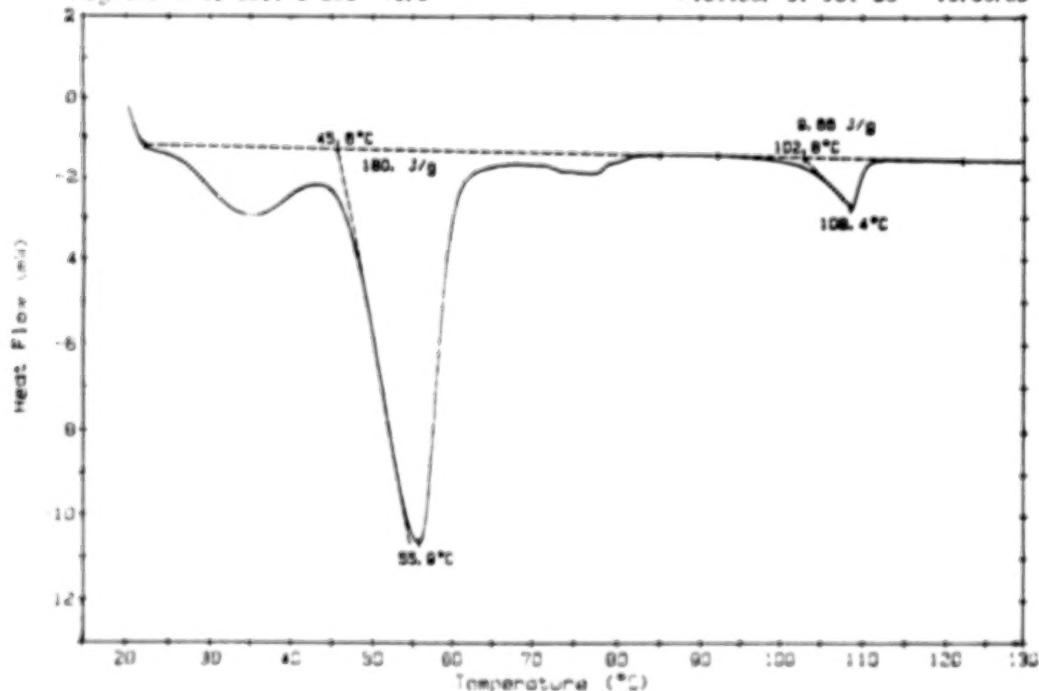
Date: 5-Aug-85 Time: 13:56:50
 File: TGA.13 TGA.7JULY.1985
 Operator: L. SKEWES
 Plotted: 5-Aug-85 15:44:12



Sample: RM-1-PARAFFIN LOW CARNUBA
 Size: 13.41 mg
 Rate: 50/MIN ARG
 Program: Interfaced DSC V3.0

DSC

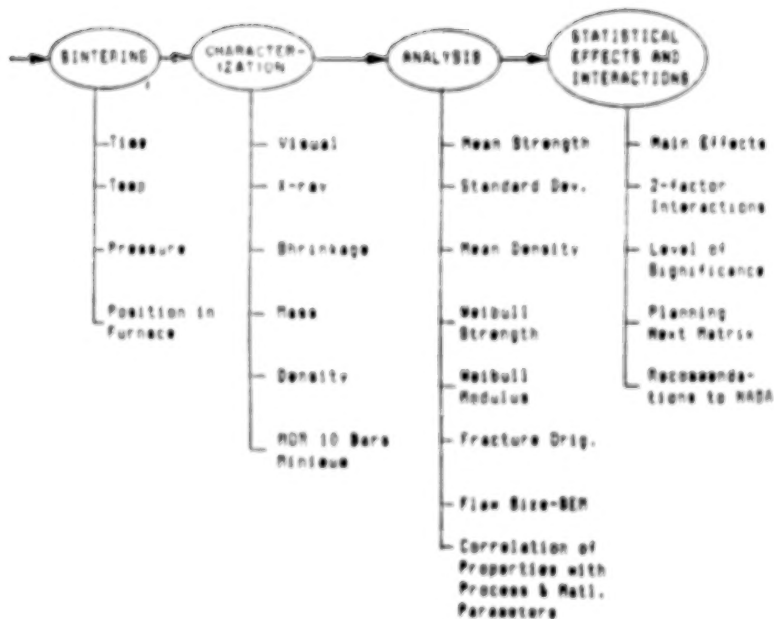
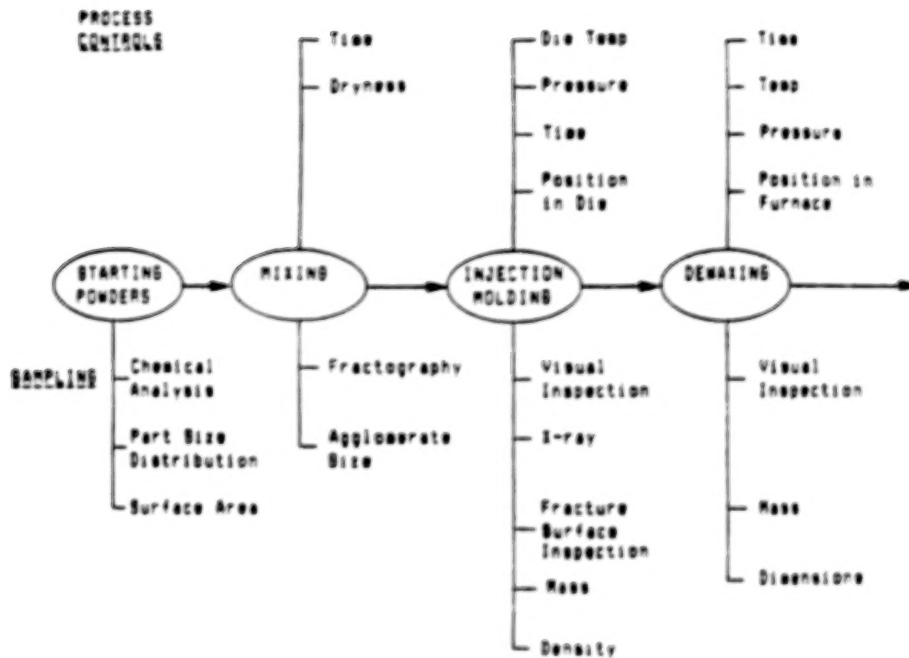
Date: 30-Jul-85 Time: 13:23:47
 File: DSC.03 DSC.3JULY85
 Operator: L. SKEWES
 Plotted: 31-Jul-85 15:45:29



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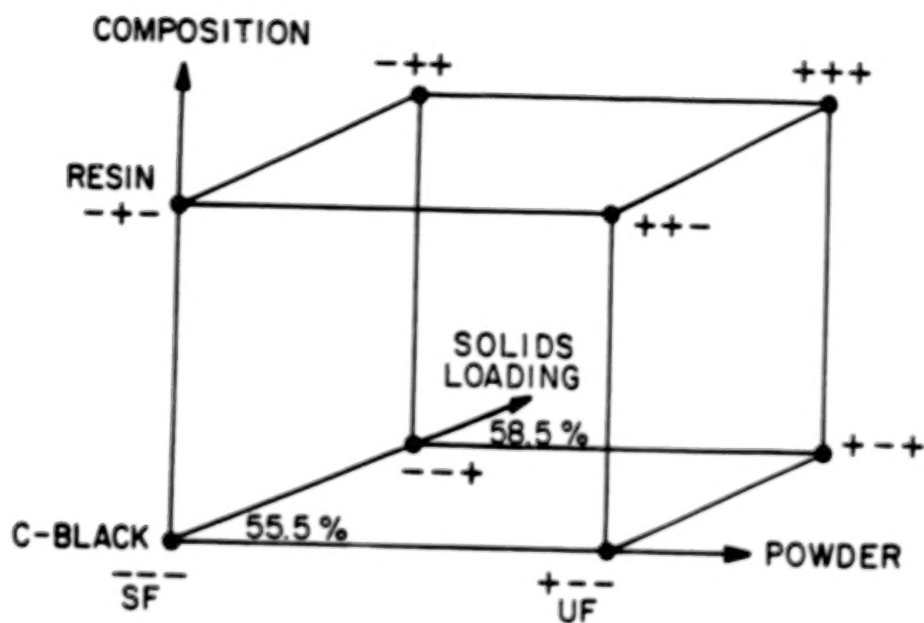
TASK I

BASELINE CHARACTERIZATION PROCESS



2³ EXPERIMENT TO

DETERMINE BASELINE COMPOSITION



2³ BASELINE EXPERIMENT

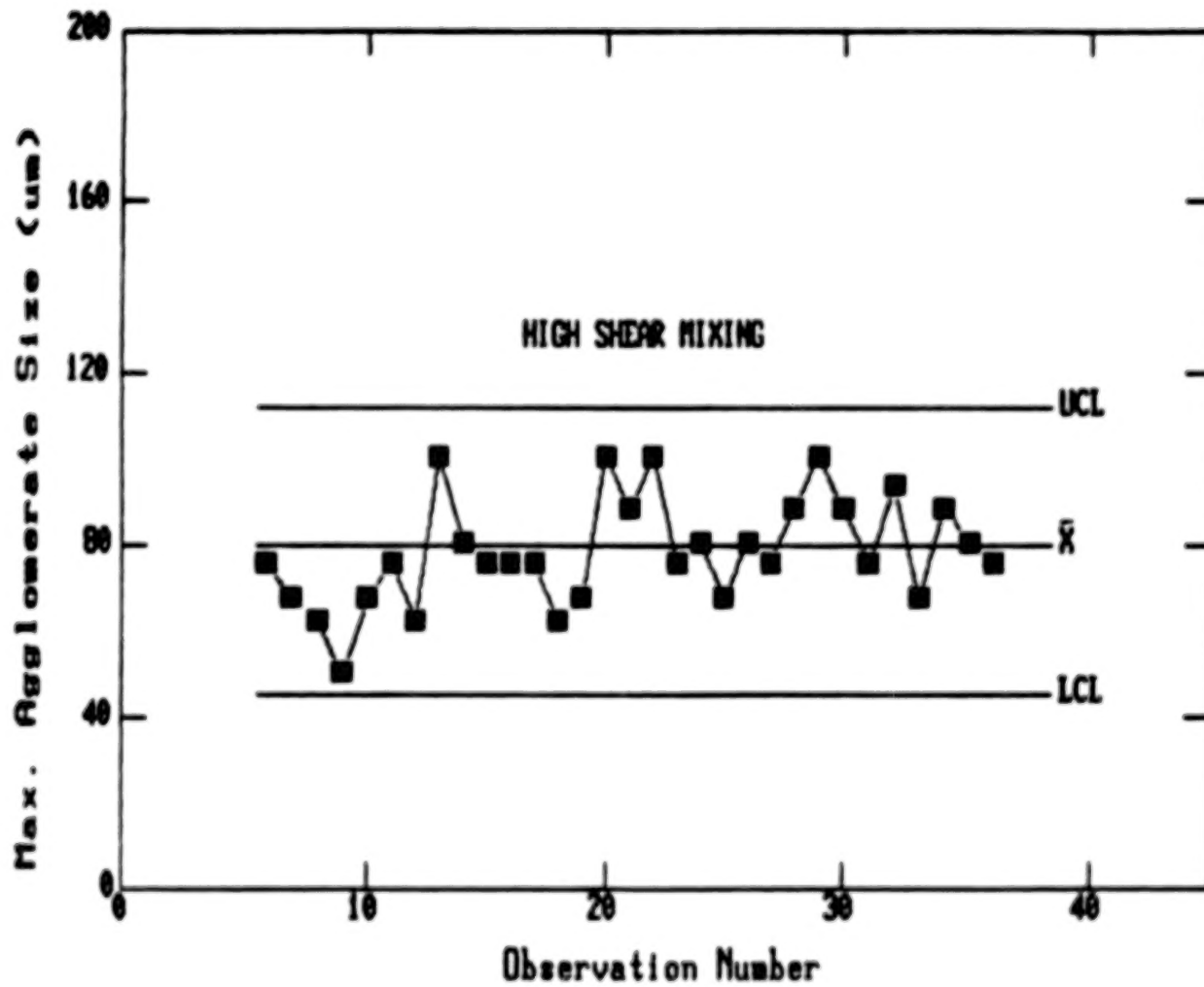
<u>NABA #</u>	<u>SOLIDS LOADING LEVEL</u>	<u>CARBON SOURCE</u>	<u>SIC SOURCE</u>	<u>XT. D.</u>
4	55.5	C-BLACK	UF	93
	58.5			94
5	55.5	C-BLACK	SF	91
	58.5			90
7	55.5	RESIN	UF	88
	58.5			--
8	55.5	RESIN	SF	88
	58.5			88

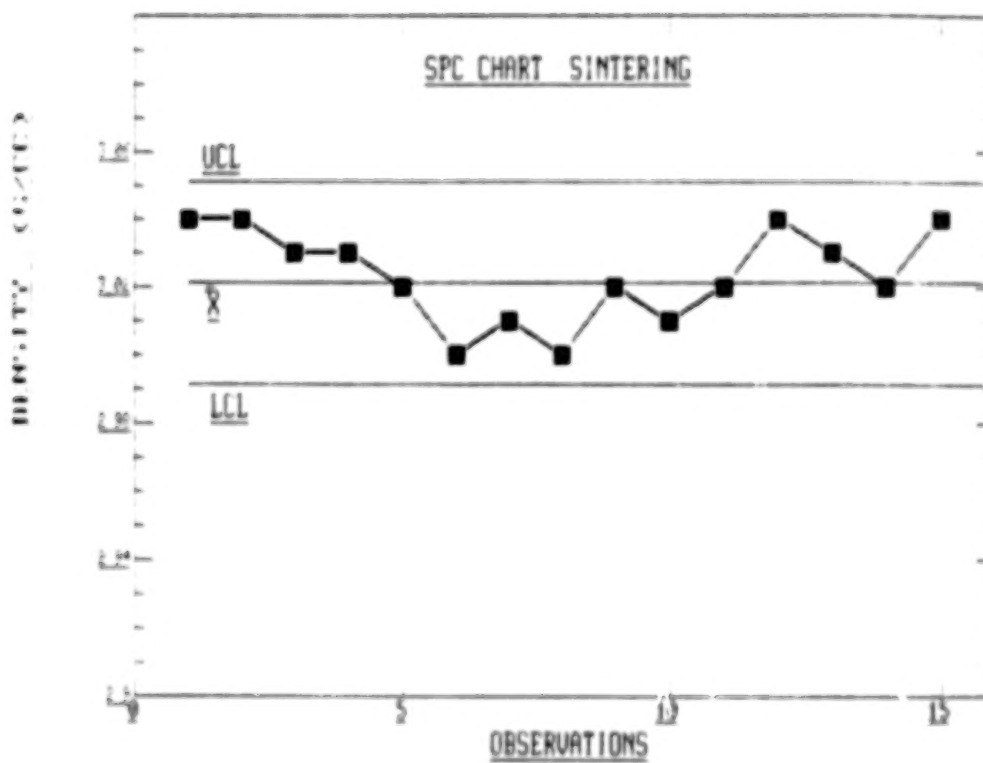
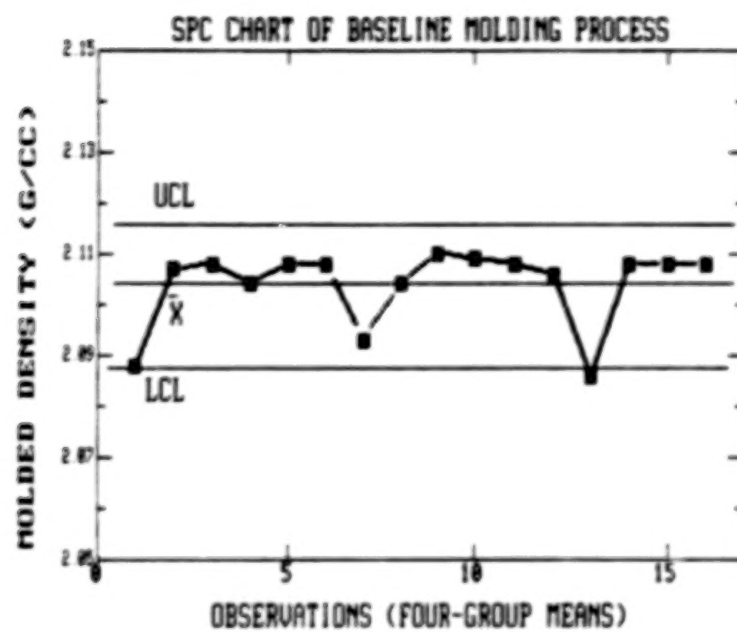
BASELINE COMPOSITION

(From 2³ Experiment)

2% C - 1%B - 97% SiC

55.5% Solids Loading





NASA 48 BASELINE
FRACTOGRAPHY AND X-RAY

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<u>M.O.R. BARS</u>			<u>FRACTURE ORIGIN</u>	<u>X-RAY</u>
<u>n</u>	<u>Ksi</u>	<u>B.D.</u>		
5	39.9	6.2	3 - Sub Surface Porosity 2 - Surface Porosity	Large inclusions, Comp. Surface
5	41.1	5.3	4 - Sub Surface Porosity 1 - Surface Porosity	Large inclusions, Center Line
5	37.3	6.7	3 - Sub Surface Porosity 2 - Surface Porosity	Clean
5	42.3	3.9	3 - Sub Surface Porosity 2 - Surface Porosity	Small inclusions

M.O.R. BASELINE SUMMARY

Molded		276*
X-ray acceptable		210
Dewaxed (1 run)		127
Sintered (3 runs)		122
Room Temp. M.O.R.		30
1000°C	FF SR	6 6 (est)
1200°C	FF SR	6 6 (est)
1400°C	FF SR	6 6 (est)

* Number of M.O.R. Bars
FF Fast Fracture Test
SR Stress Rupture Test

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TASK I

BASLINE CHARACTERIZATION

H.O.R. Results

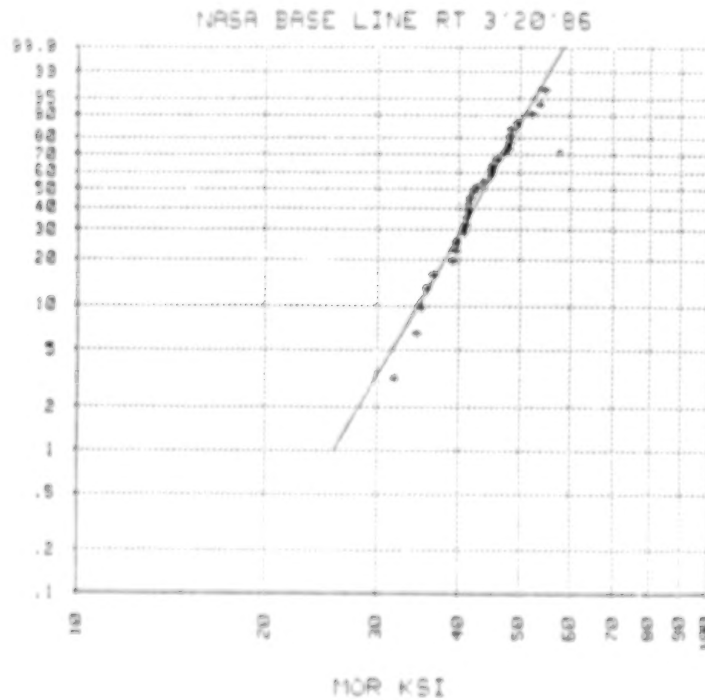
H.O.R. BASELINE RESULTS

	RT	1000°C	1200°C	1400°C
K_{01}	43.3	41.4	43.2	47.2
mPa	(299)	(285)	(298)	(325)
n	30	6	6	6
K_{01}	45.8	WEIBULL SAMPLES TOO SMALL FOR ACCEPTABLE ACCURACY		
mPa	(315)			
n	8			

	PROB. OF FAILURE	EXPECTED VALUE
NOR KSI	1.00	25.72
	10.00	34.55
	50.00	43.76
	63.00	45.79
	90.00	50.00
	95.00	52.59
	99.00	55.91
	99.90	58.41

NUMBER OF SAMPLES = 30.00
WEIBULL CHARACTERISTIC VALUE = 45.02
WEIBULL SLOPE = 7.97
DISTRIBUTION MEAN = 43.14
STANDARD DEVIATION = 6.43

WEIBULL PROBABILITY PLOT
PERCENT FAILURE



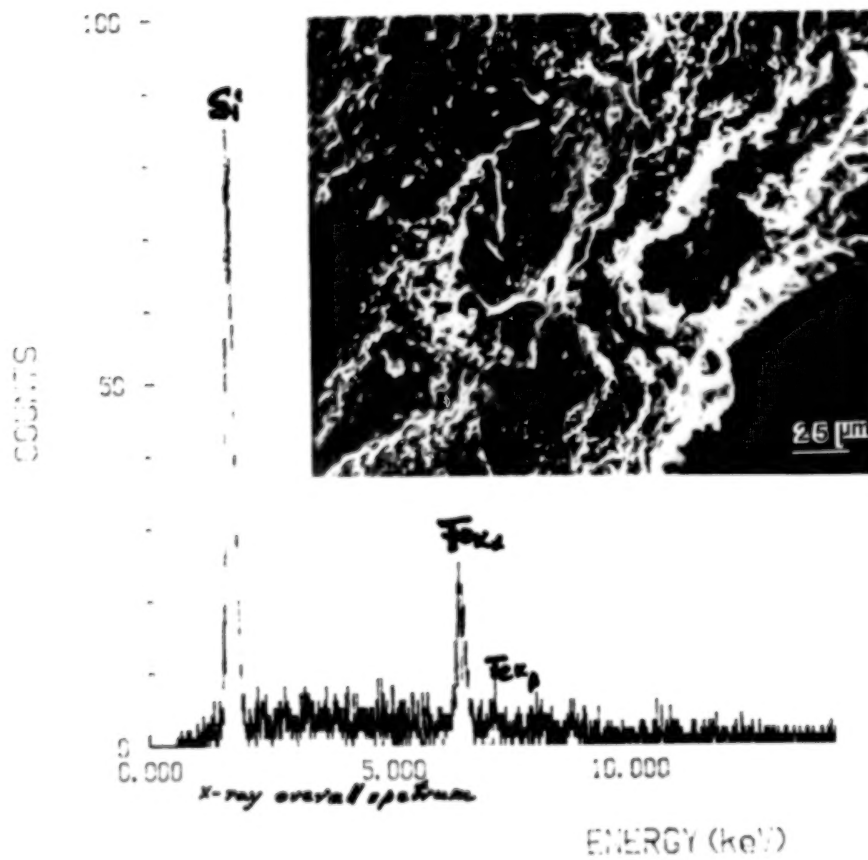
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**FRACTURE SURFACE
FLAW ORIGIN — IRON RICH**

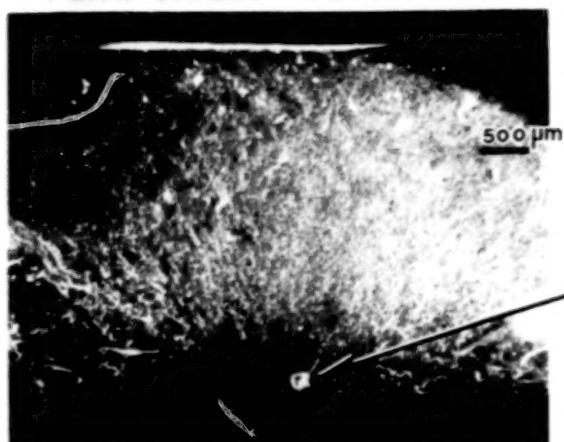


← FRACTURE ORIGIN

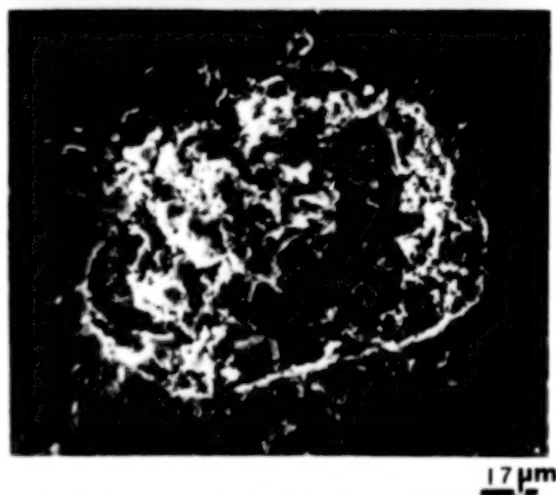
LT- 300 SECS



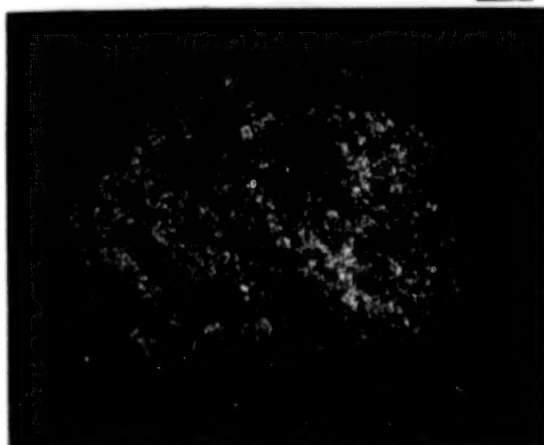
**FRACTURE SURFACE
FLAW ORIGIN — BORON RICH**



FRACTURE ORIGIN



FLAW

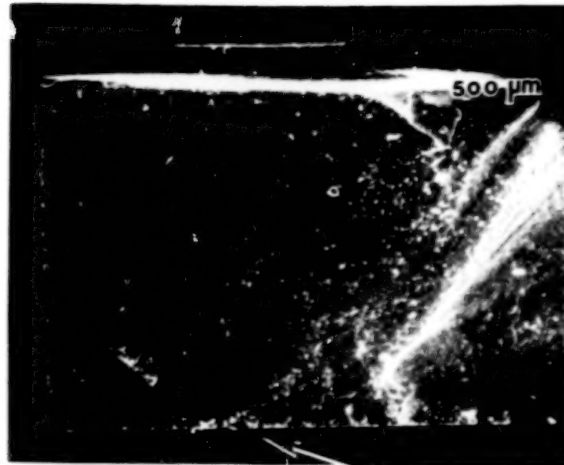


BORON MAP

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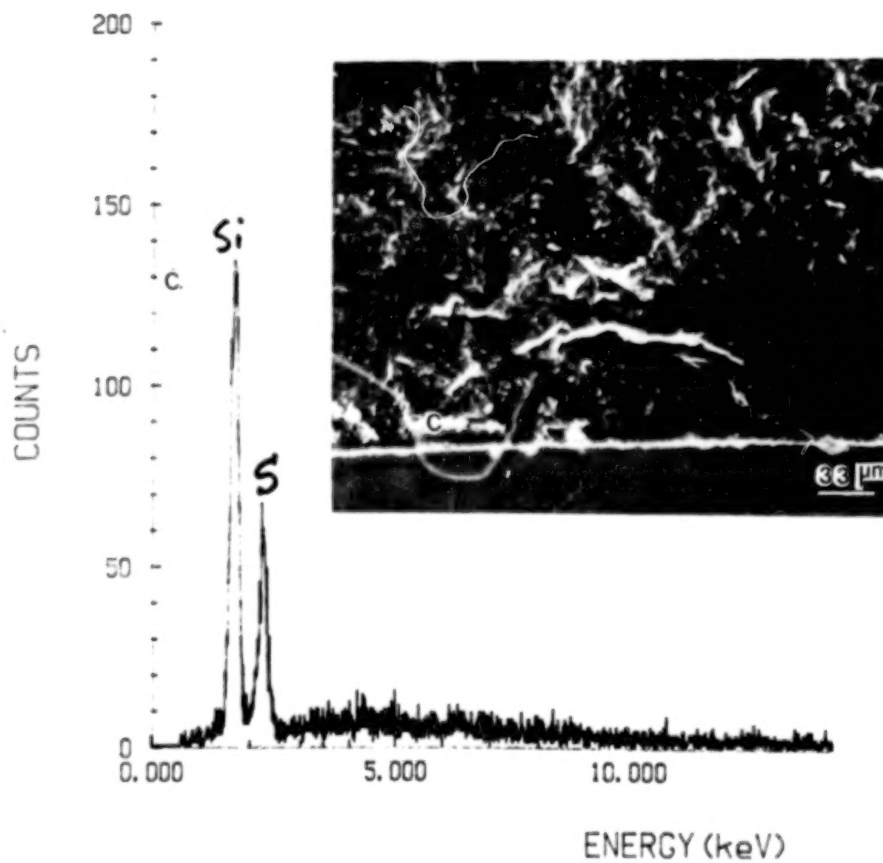
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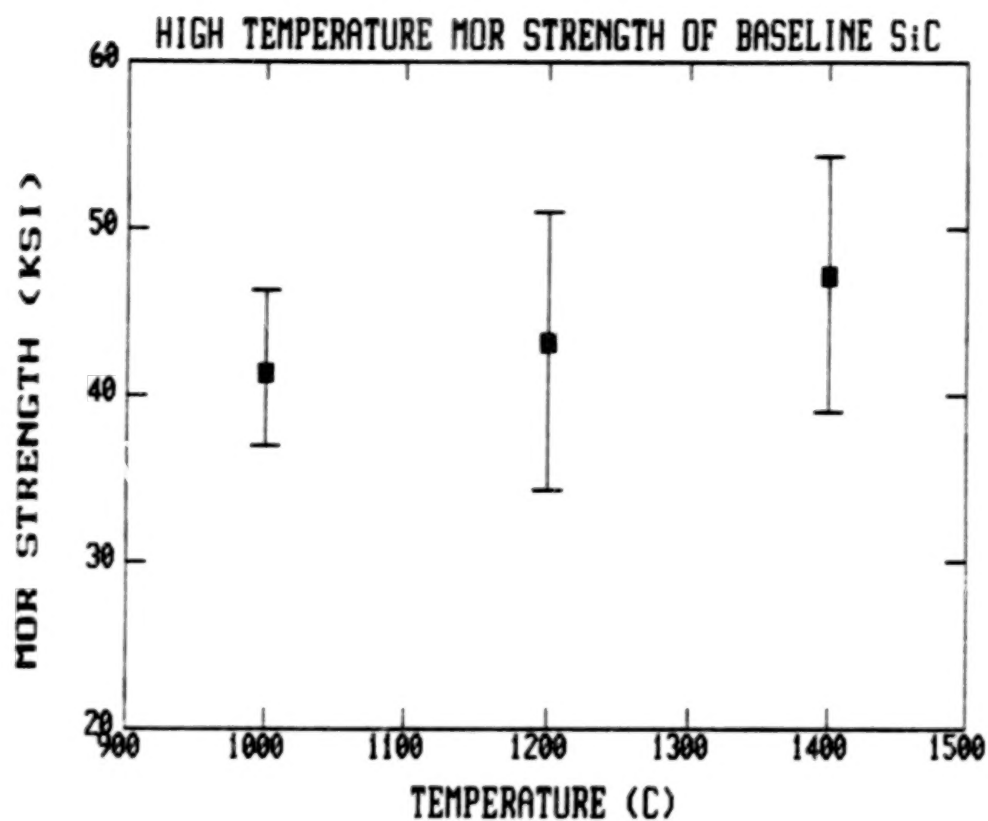
**FRACTURE SURFACE
FLAW ORIGIN - SULFUR RICH**



L1 = 300 SECS

FRACTURE ORIGIN





TASK VII

OBJECTIVE:

CONTINUOUS THROUGHOUT THE PROGRAM

**"ADVANCE THE STATE OF THE ART OF
SiC TECHNOLOGY"**

PROVIDE INPUT TO TASKS I AND II

**WAYS TO IMPROVE THE STRENGTH OF A
CERAMIC...**

$$\sigma \propto K_I E / c^{1/2}$$

**INCREASE THE FRACTURE TOUGHNESS
(MICROSTRUCTURE)**

**INCREASE THE ELASTIC MODULUS
(DENSITY) ****

REDUCE THE FLAW SIZE **

**** ADDRESSED IN TASK VII**

**INJECTION MOLDED SiC
PROCESS FLOW SHEET**

POWDER PREPARATION

**BLEND SINTERING ADDITIVES
WITH SiC ****

**MIX SOLIDS WITH INJECTION MOLDING
BINDERS ****

INJECTION MOLD **

BINDER REMOVAL **

SINTER **

MACHINE

STRENGTH EVALUATION

**** ADDRESSED IN TASK VII**

**DEVELOPMENT OF IMPROVED MIXING
TECHNIQUES**

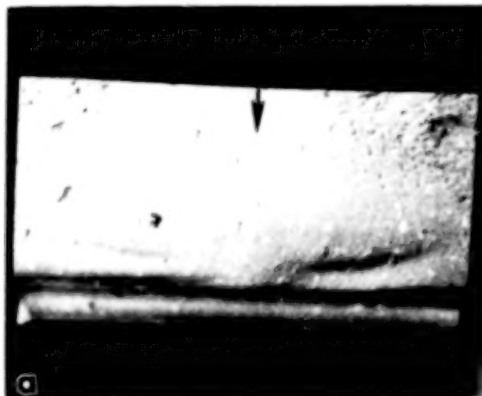
**FRACTURE ORIGINS IDENTIFIED AS
PROCESSING FLAWS**

**FLAWS IDENTIFIED AS AGGLOMERATES IN
THE INJECTION MOLDING BATCH**

**AGGLOMERATES WERE DETECTED IN THE
"MIXING" STAGE OF THE PROCESS**

"GREEN" INJECTION MOLDED TEST BARS

**STRENGTH CONTROLLING AGGLOMERATES
(UF POWDER)**



**NO AGGLOMERATES OBSERVED
(SF POWDER)**



1 mm

**ORIGINAL PAGE IS
OF POOR QUALITY**

**DRY MIXING PROCESS
(METHOD 1)**

POWDER PREPARATION

DRY BLEND SINTERING ADDITIVES
WITH SiC

MIX SOLIDS WITH INJECTION MOLDING
BINDER USING DOUBLE PLANETARY
MIXER **

INJECTION MOLD **

** AGGLOMERATES OBSERVED

**DRY MIXING PROCESS
(METHOD 2)**

POWDER PREPARATION

DRY BLEND SINTERING ADDITIVES
WITH SiC

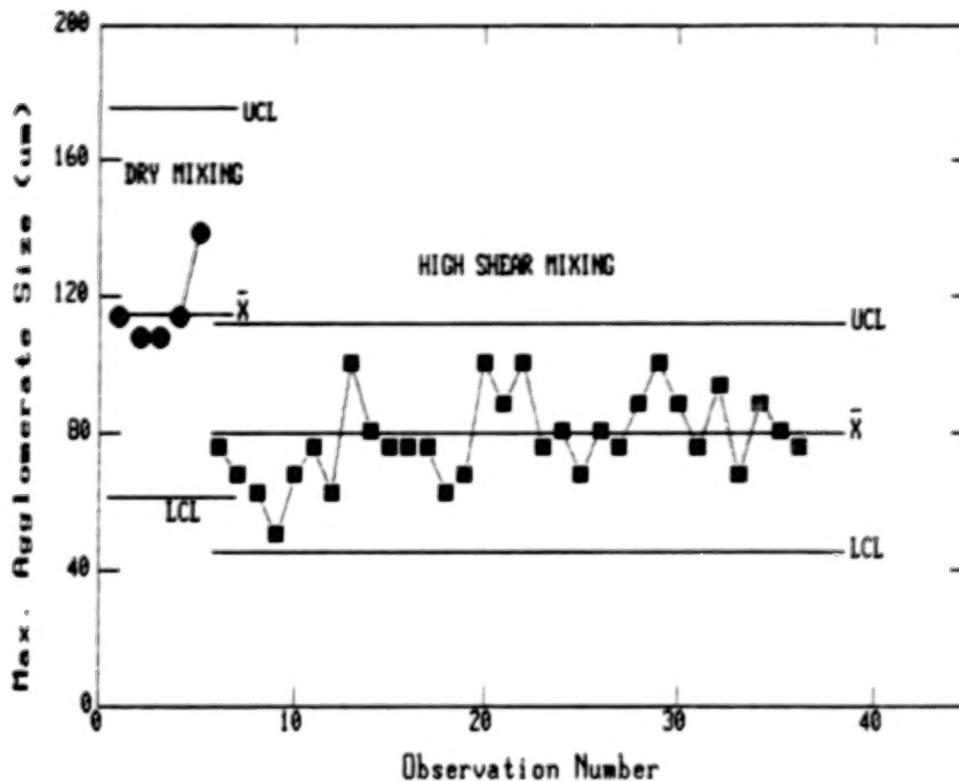
MIX SOLIDS WITH INJECTION MOLDING
BINDER USING DOUBLE PLANETARY
MIXER **

RE-MIX MOLDING BATCH IN HIGH SHEAR
HAAKE MIXER **

INJECTION MOLD **

** AGGLOMERATES OBSERVED

**HIGH SHEAR MIXING WAS FOUND TO REDUCE
THE AGGLOMERATE SIZE**



**FLUID MIXING WAS INVESTIGATED
TO REDUCE AGGLOMERATE SIZE**

**FLUID MIXING PROCESS
(METHOD 1)**

POWDER PREPARATION

**FLUID BLEND SINTERING ADDITIVES
WITH SiC**

**FLUID BLEND SOLIDS WITH INJECTION
MOLDING BINDERS
(BINDERS DISSOLVED IN FLUID)**

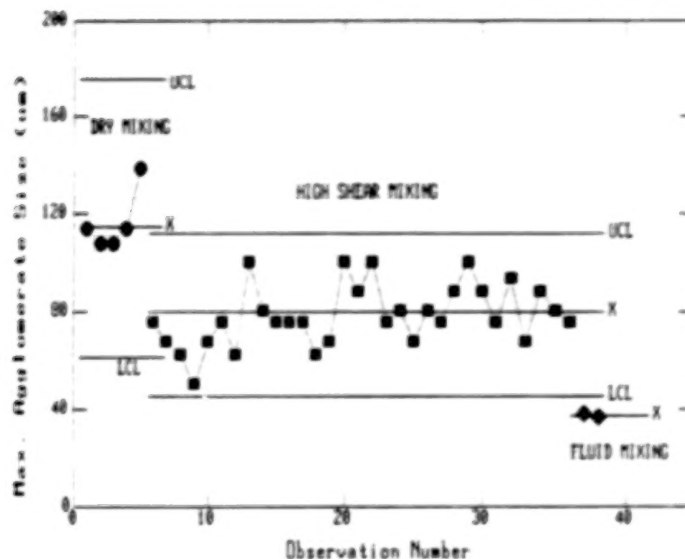
REMOVE FLUID BY DRYING

**ADD ADDITIONAL WAX USING
DOUBLE PLANETARY MIXER ****

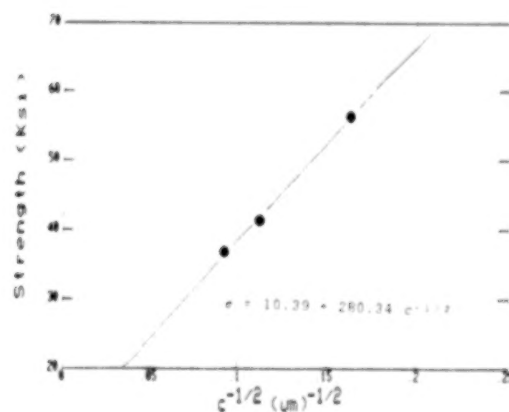
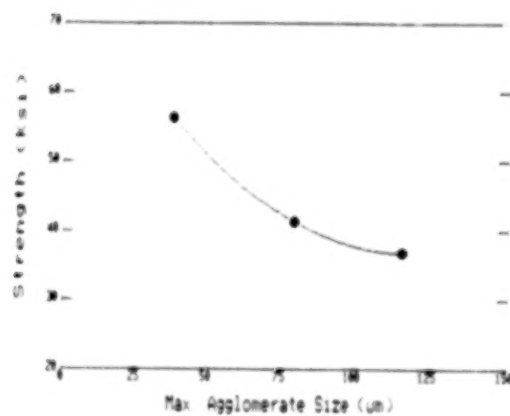
INJECTION MOLD **

**** AGGLOMERATES OBSERVED**

FLUID MIXING WAS FOUND TO FURTHER
REDUCE THE AGGLOMERATE SIZE



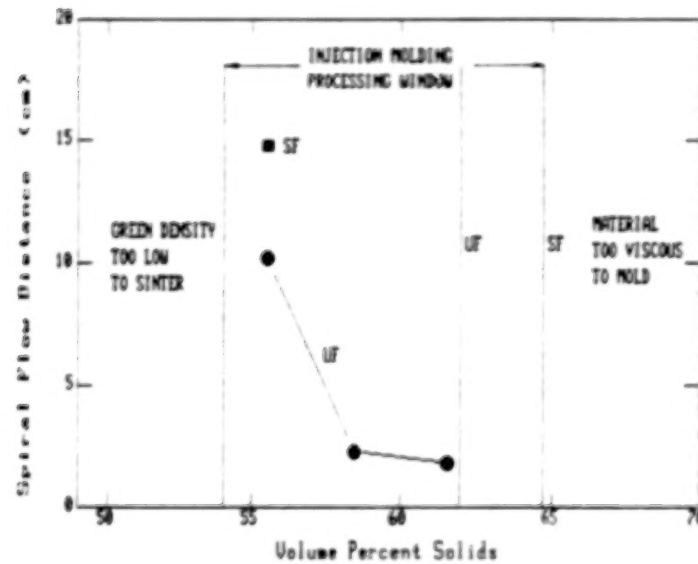
REGRESSION MODEL ILLUSTRATES THE
RELATION BETWEEN STRENGTH AND
AGGLOMERATE SIZE



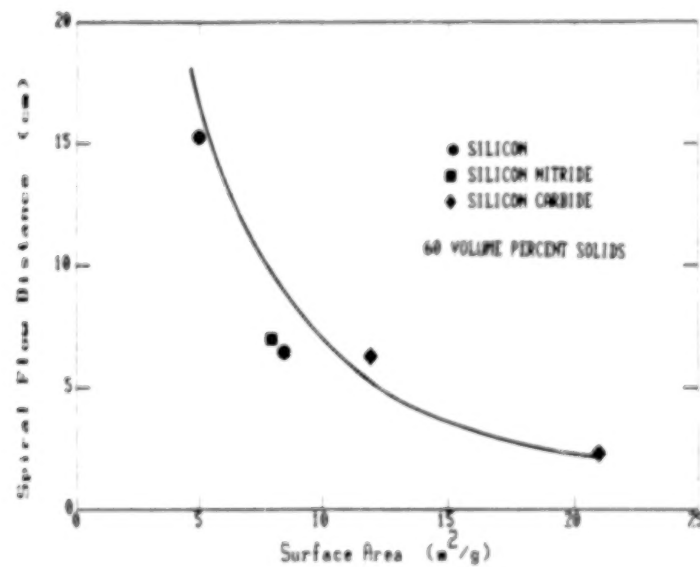
FLUID MIXING PROCESS WILL
BE USED IN THE REMAINDER
OF THE PROGRAM (TASK II)

INJECTION MOLDING

INJECTION MOLDING PROCESSING WINDOW
WAS IDENTIFIED



INJECTION MOLDING BEHAVIOR OF ALL
SILICON BASED CERAMIC POWDERS
IS A FUNCTION OF SURFACE AREA



**INJECTION MOLDING PROCESS YIELDS
WERE IMPROVED THROUGH EQUIPMENT
MODIFICATION**

COMPOSITION: 12A - 60.0 VOL % SOLIDS

ORIGINAL SYSTEM:

**332 BARS MOLDED
221 BARS VOID FREE**

66.6 % YIELD

IMPROVED VACUUM SYSTEM:

**24 BARS MOLDED
23 BARS VOID FREE**

95.8 % YIELD

BINDER REMOVAL - SINTERING

**CURRENT PROCESS USES
VACUUM FOR BINDER REMOVAL
VACUUM FOR SINTERING**

**VACUUM PROCESSING RESULTS IN CRACK
FREE TEST BARS HAVING GOOD DENSITY**

**PROBLEMS ARE ANTICIPATED WITH
VACUUM PROCESSING:**

**CRACKING IN THICK CROSS SECTION
COMPONENTS**

**LOW DENSITY AREAS ON AS SINTERED
SURFACES**

EXPERIMENTS WERE INITIATED TO
INVESTIGATE ALTERNATIVES TO VACUUM
PROCESSING DURING BINDER REMOVAL
AND SINTERING.

BINDER REMOVAL

2nd EXPERIMENTAL DESIGN

VARIABLES:
HEATING RATE
PRESSURE

EXP.		PERCENT BINDER REMOVAL	VACUUM SINTERED DENSITY
1)	-	91.7	93.5
2)	+	91.4	93.6
3)	-	95.8	93.5
4)	+	96.4	93.8

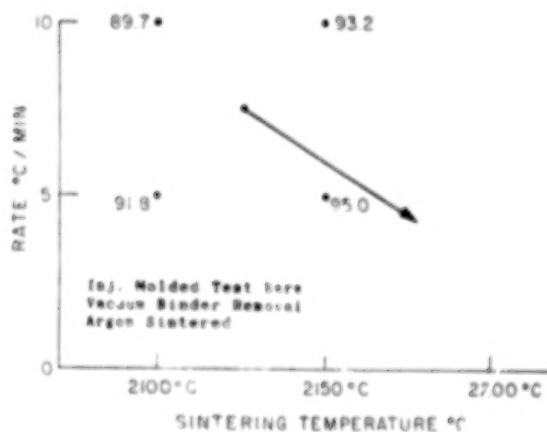
EXP. 1 USED FOR BASELINE PROCESSING

EXP. 3 OFFERS POTENTIAL FOR
PROCESSING LARGE COMPONENTS

SINTERING

ARGON SINTERING POTENTIAL
DEMONSTRATED

SINTERED DENSITY VS SINTERING VARIABLES



FUTURE PLANS

TASK II

$$\sigma \propto K_I E / c^{1/2}$$

FIRST ITERATION:

**REDUCE PROCESSING FLAW SIZE
(AGGLOMERATES)**

SECOND ITERATION:

INCREASE DENSITY (ELASTIC MODULUS)

**OPTIMIZE MICROSTRUCTURE (INCREASE
FRACTURE TOUGHNESS)**

FUTURE PLANS

TASK VII

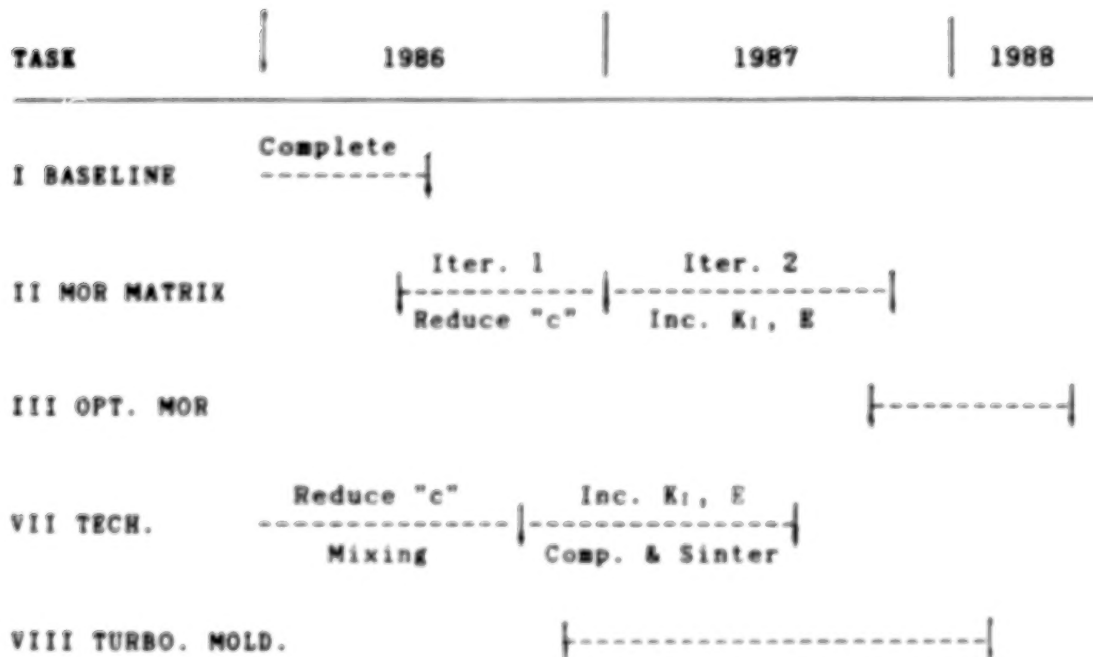
**CONTINUE TO STUDY WAYS TO REDUCE
AGGLOMERATE SIZE**

**CONTINUE TO INVESTIGATE BINDER
REMOVAL TECHNIQUES**

**CONTINUE TO STUDY THE INTERRELATION
BETWEEN BINDER REMOVAL AND SINTERING**

**INITIATE WORK TO INCREASE SINTERED
DENSITY AND IMPROVE SINTERED
MICROSTRUCTURE**

PROGRAM TIMING CHART PHASE I



N88-23880

P-10

STRENGTH OPTIMIZATION OF α -SiC BY IMPROVED PROCESSING

Sunil Dutta
NASA Lewis Research Center
Cleveland, Ohio 44135

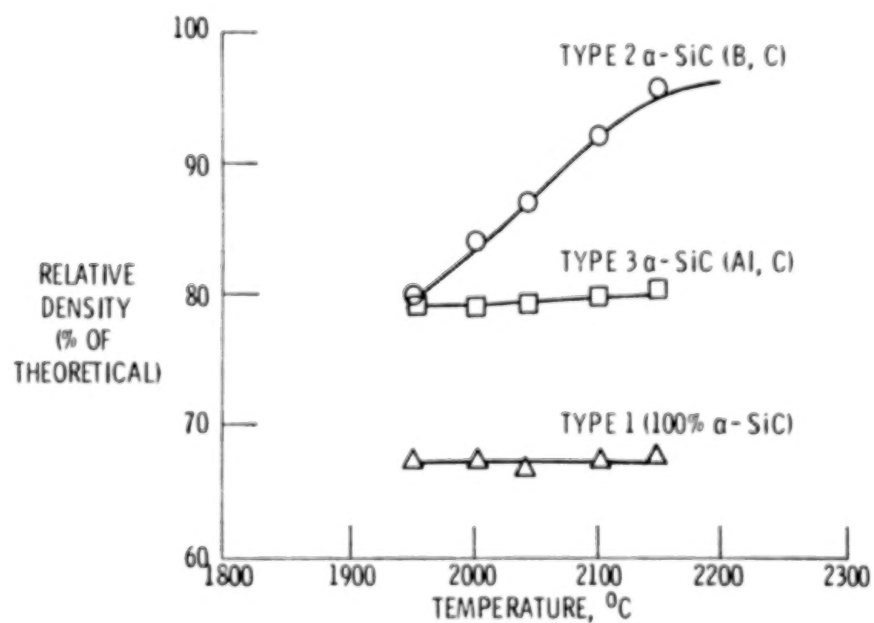
Silicon carbide is of great interest for structural use in aircraft and automobile engines. This ceramic combines high thermal conductivity and low coefficient of thermal expansion, and consequently has good thermal shock resistance. However, like other ceramics, silicon carbide shows strength variability due to processing flaws such as large voids, shrinkage cracks, inclusions, etc. Agglomerates in the starting powder seem to be the predominant cause for such defects. Improved processing techniques such as slurry pressing and hot isostatic pressing were employed to minimize these defects and to improve strength and reliability in the fabricated material. For this purpose 2-inch diameter discs were fabricated by various consolidation techniques. These include: (1) dry pressing and sintering, (2) slurry pressing and sintering, and (3) slurry pressing and HIPing. High density (>96 percent of theoretical) was produced by sintering at 2150 - 2200 °C. By contrast, a much lower temperature (1850-1900 °C) was required by HIPing to achieve high final density specimens. Dry pressing and sintering yielded an average flexure strength (4-point bend) of 350 MPa (50 ksi), while slurry pressing and sintering produced an average strength of 430 MPa (62 ksi), a 30 percent improvement in strength. Further, slurry pressing and HIPing yielded an average strength of 580 MPa (84 ksi). This strength value is 60 percent higher than the dry-pressed/sintered strength, and 30 percent higher than the slurry-pressed/sintered strength. The HIP silicon carbide exhibited an ultrafine grained microstructure (0.3-3 μ m) as compared to 1-30 μ m produced by sintering. Process related defects such as large isolated voids, shrinkage cracks, etc. were not observed in HIPed silicon carbide.

TABLE 1 ANALYSIS OF AS-RECEIVED α - SiC POWDERS

ELEMENT	IMPURITY ANALYSIS (PPM)		
	TYPE 1	TYPE 2	TYPE 3
	α - SiC (100%)	α - SiC (B, C)	α - SiC (Al, C)
Al	50	140	12 ^a
Ca	70	40	20
Fe	10	10	40
Ti	20	30	50
V	20	20	40
B	-	0.60 ^a	-
FREE C	1.66 ^a	7.31 ^a	6.10 ^a
SURFACE AREA (BET) m ² /gm	31.47	4.19	11.38

^aWT PERCENT

CD-86-19198

RELATIVE DENSITY OF THREE TYPES OF STARCK α -SiC POWDER
SINTERED FOR 30 min AT DIFFERENT TEMPERATURES

V-1270

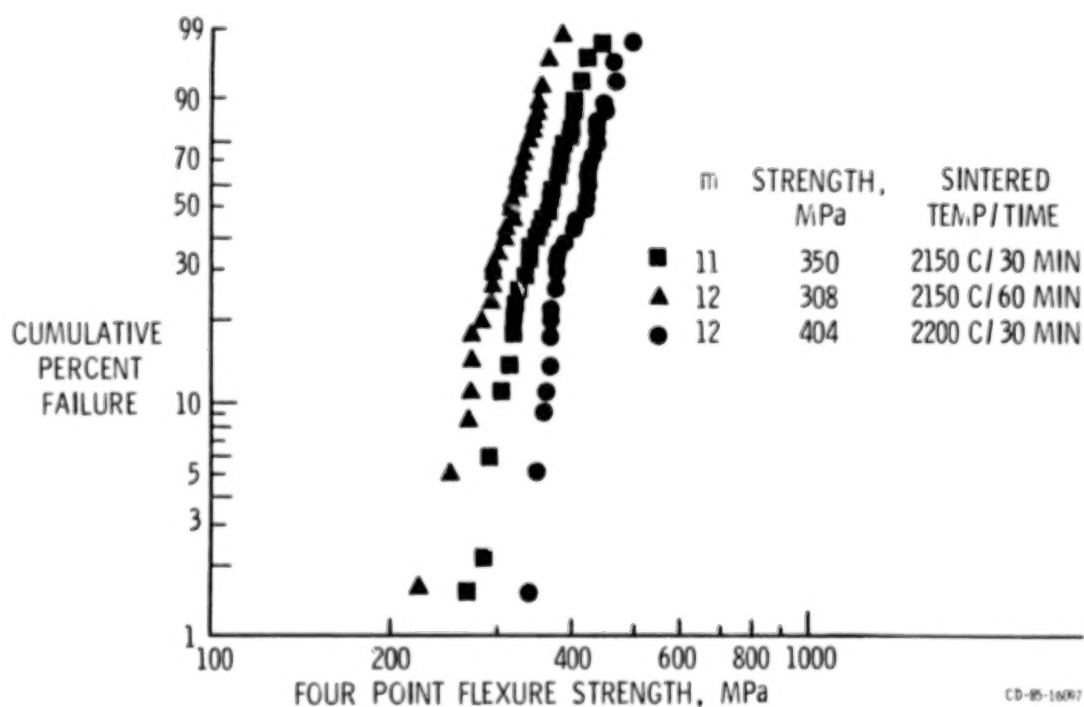
CS-83-1723

PROCESSING AND PROPERTIES OF TYPE 2 (AS-RECEIVED) α - SiC (B, C) MATERIAL

α - SiC TYPE	SINTERED TEMPERATURE, °C	TIME, min	DENSITY, g/cm ³	MOR/TEST TEMPERATURE,	NUMBER OF SPECIMEN	MEAN MOR/ δ -D, MPa	WEIBULL/R ² , m
2	2150	30	95	RT	23	353/	11/95
2	2150	60	96	RT	28	306/32	12/97
2	2200	30	97	RT	30	404/40	12/89
2	2150	30	95	1370	20	312/	7/97
2	2150	60	96	1370	24	265/32	10/94
2	2200	30	97	1370	30	316/53	7/80

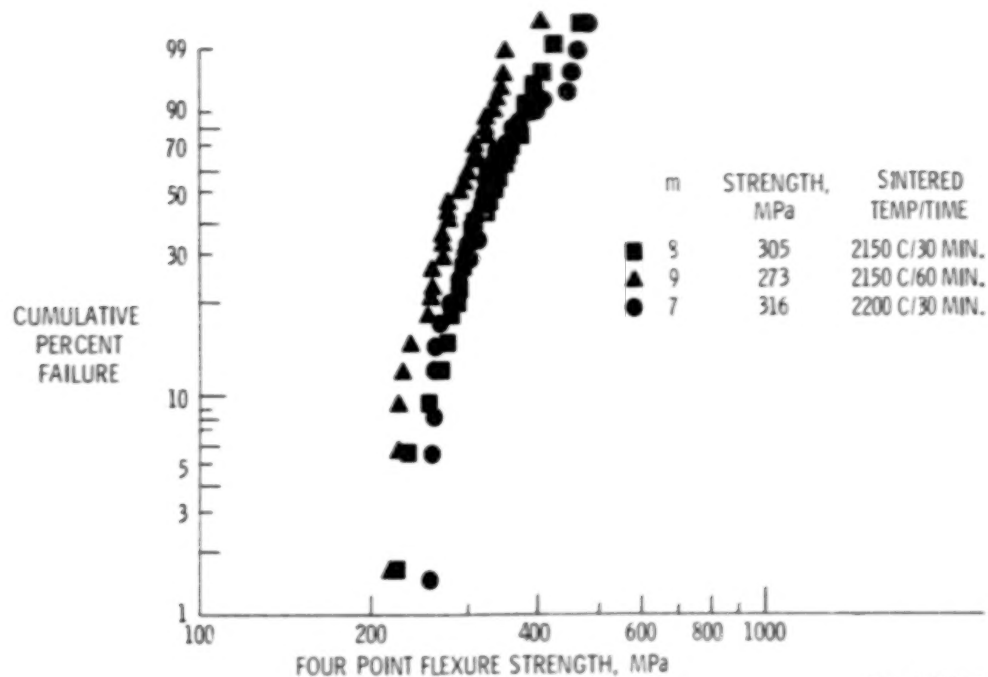
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WEIBULL PROBABILITY CHART FOR ROOM TEMPERATURE FRACTURE OF STARCK TYPE 2 α - SiC (B, C)



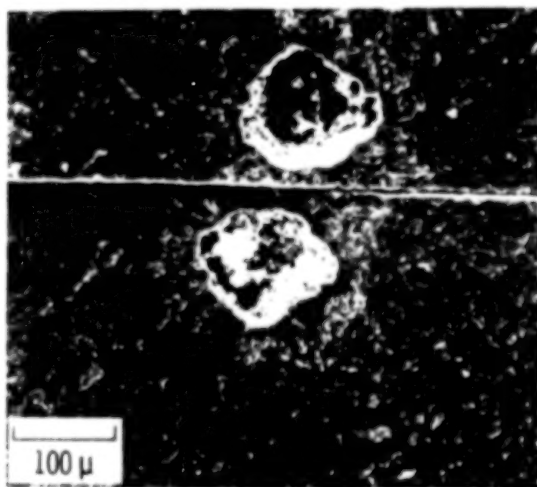
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WEIBULL PROBABILITY CHART FOR 1370° C FRACTURE OF STARCK TYPE 2 α -SiC (B, C)

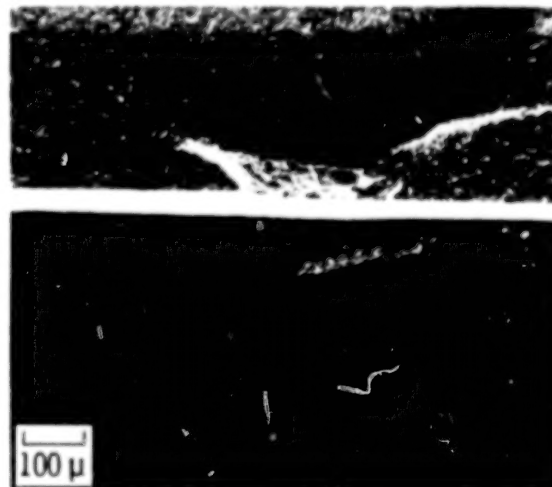


CD-85-16178

ROOM TEMPERATURE FRACTURE OF DRY-PRESSED/SINTERED α -SiC



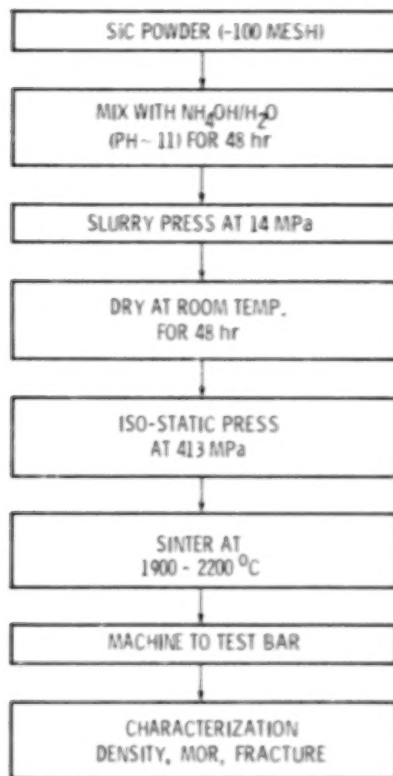
σ_f -227 MPa



σ_f -225 MPa

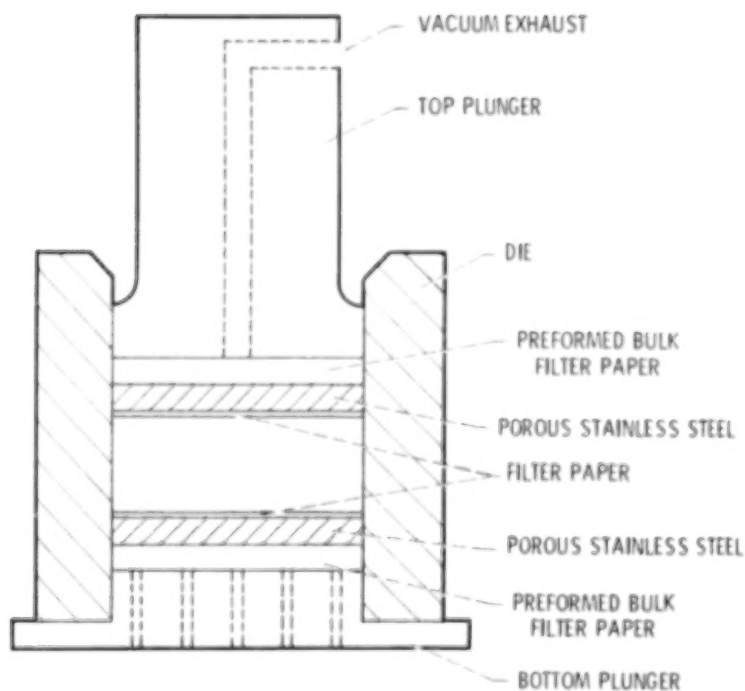
CD-86-19188

SLURRY-PRESSING FLOW DIAGRAM



CD-86-19200

SCHEMATIC OF SLURRY PRESSING APPARATUS



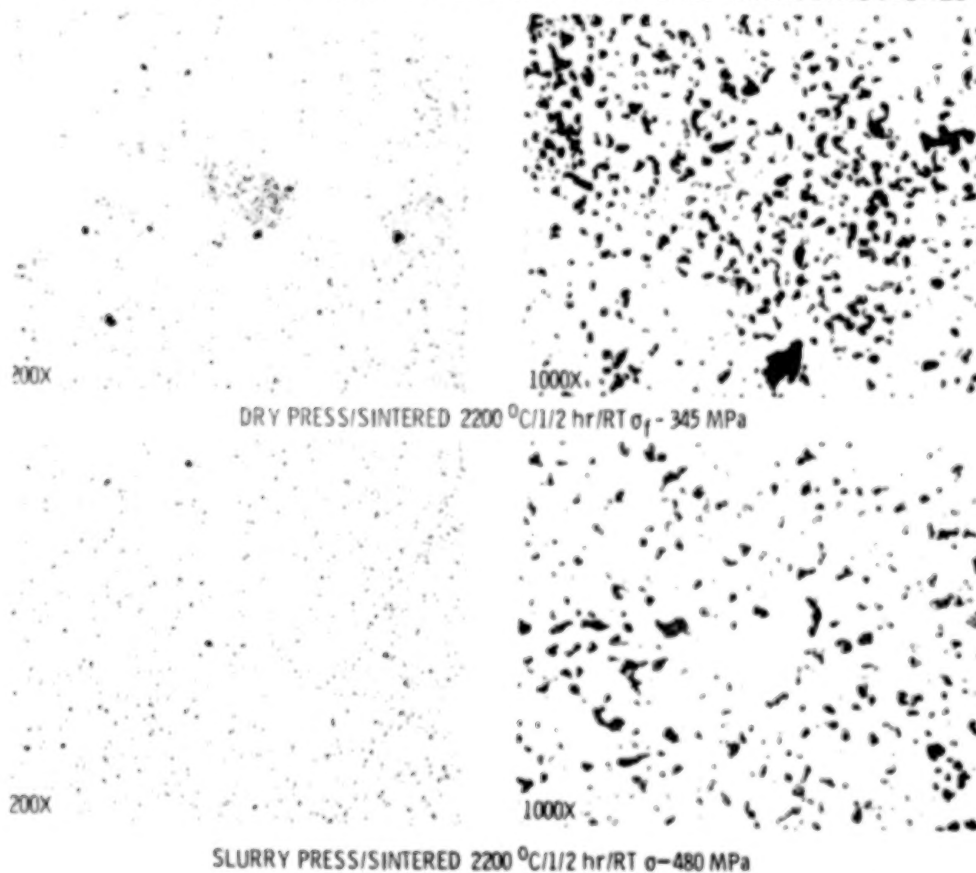
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PROPERTIES OF SINTERED VS HOT ISOSTATIC PRESSED α - SiC

α - SiC TYPE	PROCESSING METHOD	DENSIFICATION TEMPERATURE, $^{\circ}$ C	TIME, min	DENSITY (% OF THEORETICAL)	MEAN MOR/6-D MPa	NO. OF SPECIMEN	WEIBULL/ R^2 m
2	DRY PRESS/ SINTERED	2200	30	97.4	342 $\pm$ 52.8 (49.6 $\pm$ 5.7 ksi)	30	8
2	SLURRY PRESS/ SINTERED	2200	30	96.5	416 $\pm$ 53.3 (60.3 $\pm$ 7.7 ksi)	22	9.3
2	SLURRY PRESS/ HIPed	1900	30	95.3	580 $\pm$ 77	15	8.8
2	SLURRY PRESS/ HIPed	1800	30	80.5	N. D.	8	N. D.

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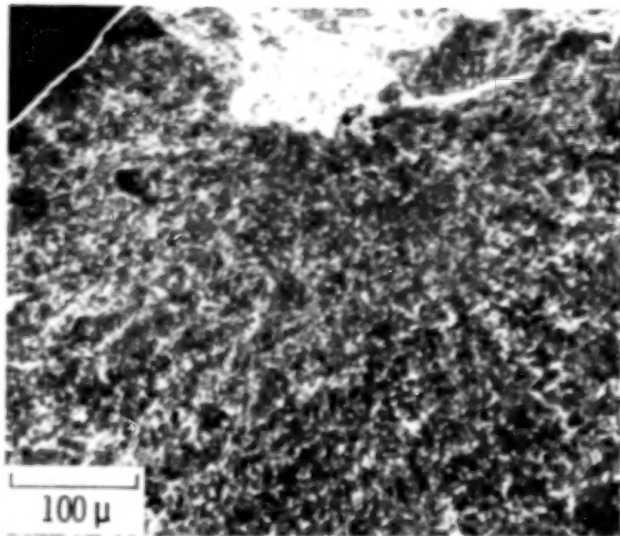
EFFECT OF DRY PRESSING VS SLURRY PRESSING ON SINTERED MICROSTRUCTURES OF α -SiC



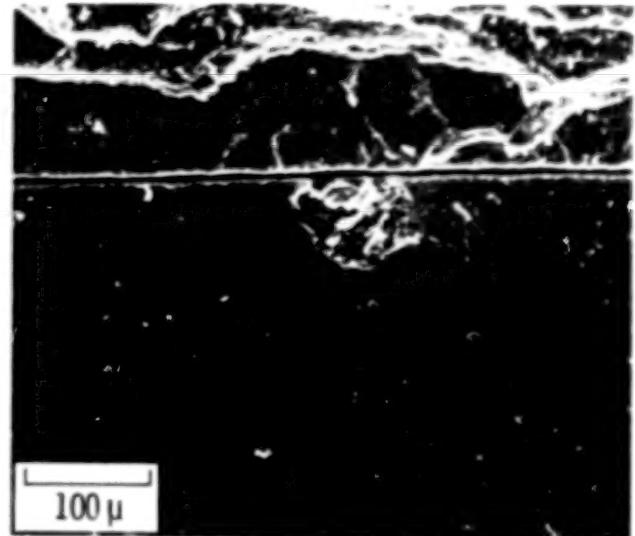
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ROOM TEMPERATURE FRACTURE OF SLURRY-PRESSED/SINTERED α -SiC



$\sigma_f - 340$ MPa



$\sigma_f - 260$ MPa

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HIPing OF STRUCTURAL CERAMICS

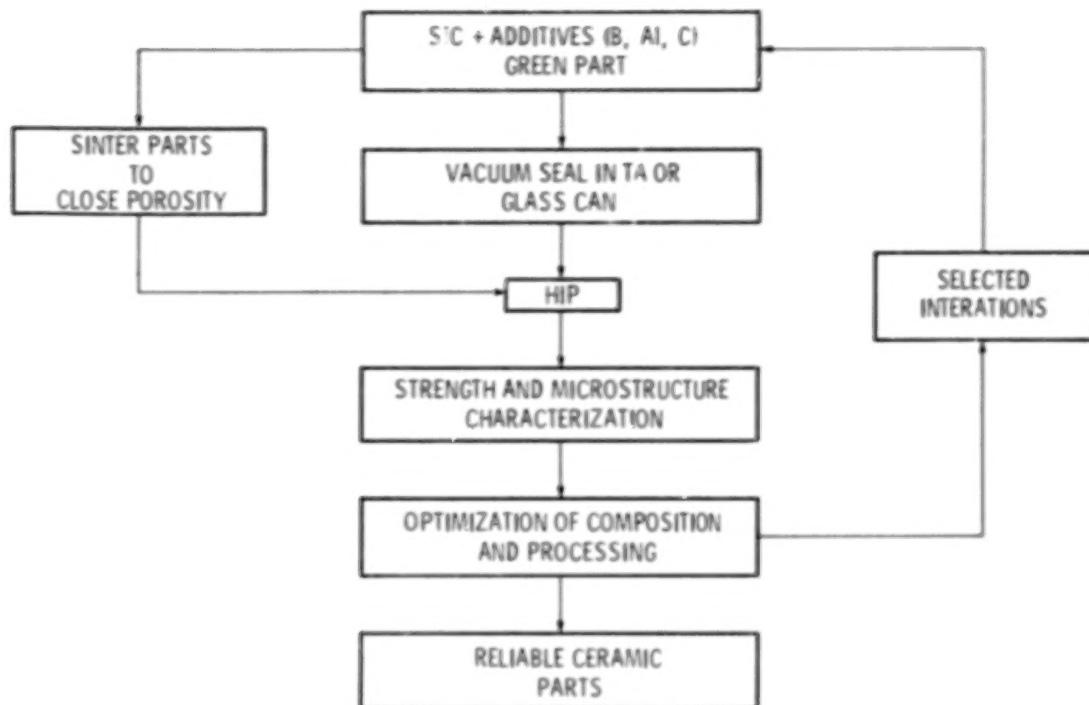
ADVANTAGES:

HOT ISOSTATIC PRESSING (HIPing) OF STRUCTURAL CERAMICS, e.g.,
 Si_3N_4 AND SiC.

- o ENHANCES DENSITY (APPROACHES TD)
- o IMPROVES MICROSTRUCTURE
- o SIGNIFICANTLY INCREASES STRENGTH
- o IMPROVES RELIABILITY

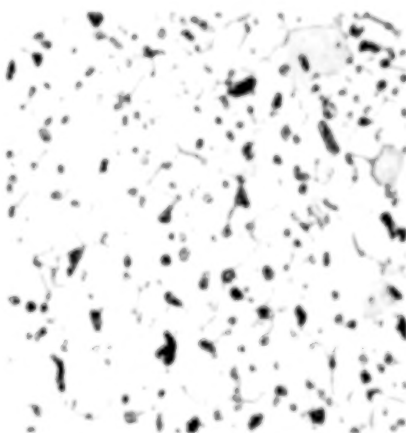
CD-86-19185

HOT ISOSTATIC PRESSING - GENERAL FLOW CHART

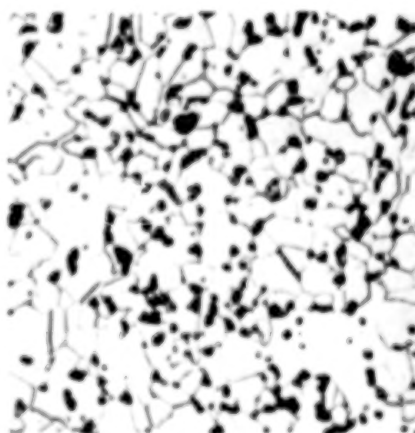


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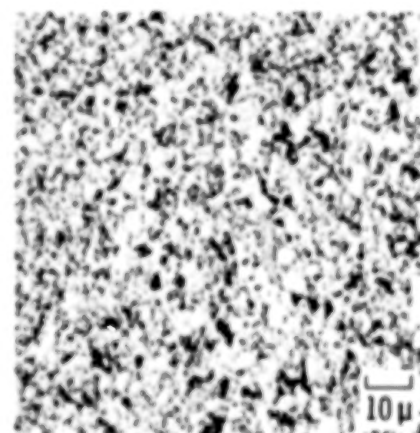
MICROSTRUCTURE DEVELOPMENT IN SINTERED AND HOT ISOSTATIC PRESSED α -SiC



DRY-PRESSED/SINTERED
2200 C / 1/2 hr



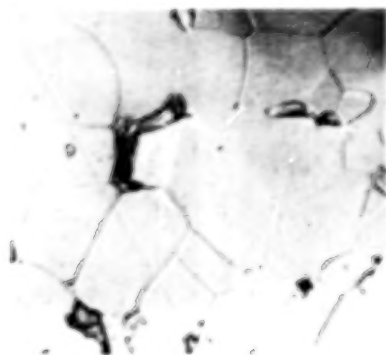
SLURRY-PRESSED/SINTERED
2200 C / 1/2 hr



SLURRY-PRESSED/HIPed
1900 C / 1/2 hr

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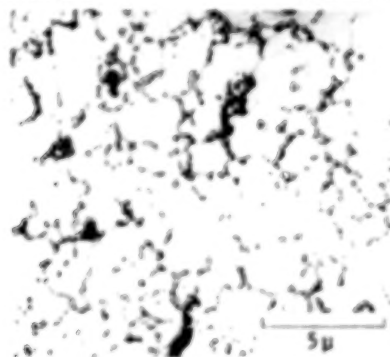
REPLICA PHOTOMICROGRAPHS OF SINTERED AND HOT ISOSTATIC PRESSED α -SiC



DRY-PRESSED/SINTERED



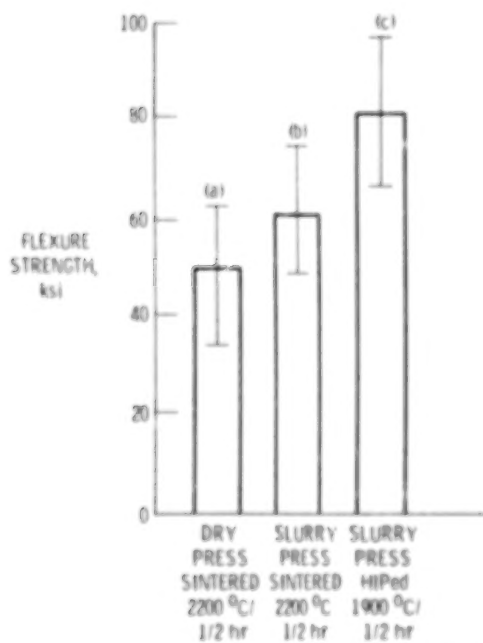
SLURRY-PRESSED/SINTERED



SLURRY-PRESSED/HIPed

CD-86-19190

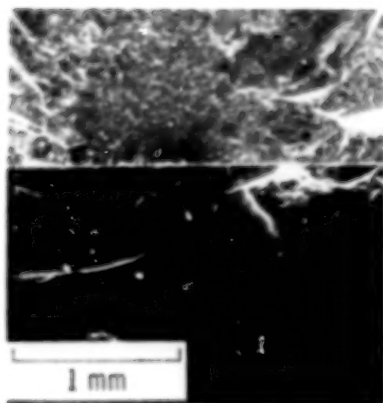
ROOM TEMPERATURE FLEXURE STRENGTH OF SINTERED VS HIPed SILICON CARBIDE



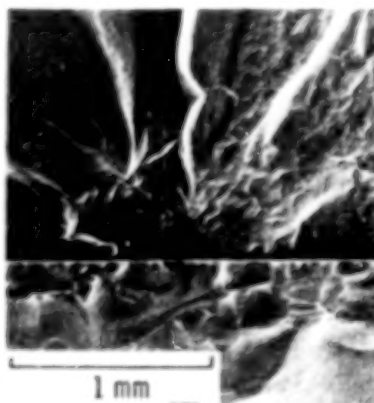
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ROOM TEMPERATURE FRACTURE OF HOT ISOSTATIC PRESSED α -SiC



σ_f - 445 MPa



σ_f - 480 MPa



σ_f - 530 MPa

CD-86-19191

CONCLUSIONS

- DRY PRESSING / SINTERING OF STARCK ALPHA SILICON CARBIDE PRODUCED HIGH DENSITY BODIES WITH AN AVERAGE FLEXURE STRENGTH (4-POINT BEND) OF 350 MPa (50 ksi).
- IN CONTRAST, SLURRY PRESSING / SINTERING PRODUCED AN AVERAGE STRENGTH OF 430 MPa (62 ksi), A 30% IMPROVEMENT IN STRENGTH.
- FURTHER, SLURRY PRESSING / HOT ISOSTATIC PRESSING (HIPing) PRODUCED HIGH DENSITY BODIES AT 1850 - 1900 °C, WITH AN AVERAGE STRENGTH OF 580 MPa (84 ksi). THIS STRENGTH VALUE IS 60% HIGHER THAN THE DRY-PRESSED / SINTERED STRENGTH, AND 30% HIGHER THAN THE SLURRY-PRESSED / SINTERED STRENGTH.
- THE SLURRY-PRESSED / HIPed MATERIAL EXHIBITED AN ULTRAFINE GRAINED (0.3 - 3 μ m) MICROSTRUCTURE AS COMPARED TO 1 - 30 μ m PRODUCED BY SINTERING.
- PROCESS RELATED DEFECTS SUCH AS LARGE VOIDS, AND SHRINKAGE CRACKS WERE NOT OBSERVED IN HIPed SILICON CARBIDE.

N88-23881 *P15*

IMPROVED SILICON NITRIDE FOR ADVANCED HEAT ENGINES

H.C. Yeh
AlResearch Casting Company *AL717*
Torrance, CA 90509

and

J.M. Wimmer
Garrett Turbine Engine Company *EH*
Phoenix, AZ

Silicon nitride is a high temperature material currently under consideration for heat engine and other applications. This presentation describes the progress made in the first 1-1/2 years of a NASA funded, 5 year program on improved Si_3N_4 . The objective of this program is to improve the net shape fabrication technology of Si_3N_4 by injection molding. This is to be accomplished by optimizing the process through a series of statistically designed matrix experiments. To provide input to the matrix experiments, a wide range of alternate materials and processing parameters were investigated throughout the whole program.

The improvement in the processing is to be demonstrated by a 20 percent increase in strength and a 100 percent increase in the Weibull modulus over that of the ACC baseline material. A full characterization of the baseline material/process was completed. The room temperature MOR and Weibull modulus of the as-processed test bars were established as 79.3 ksi and 7.9, respectively. In the first iteration of the MOR matrix experiments, a material with a room temperature MOR of 97 ksi and a Weibull modulus of 14 has been developed.

Material properties were found to be highly dependent on each step of the process. Several important parameters identified thus far are the starting raw materials, sinter/HIP cycle, powder bed, mixing methods, and sintering aid levels.

OBJECTIVES

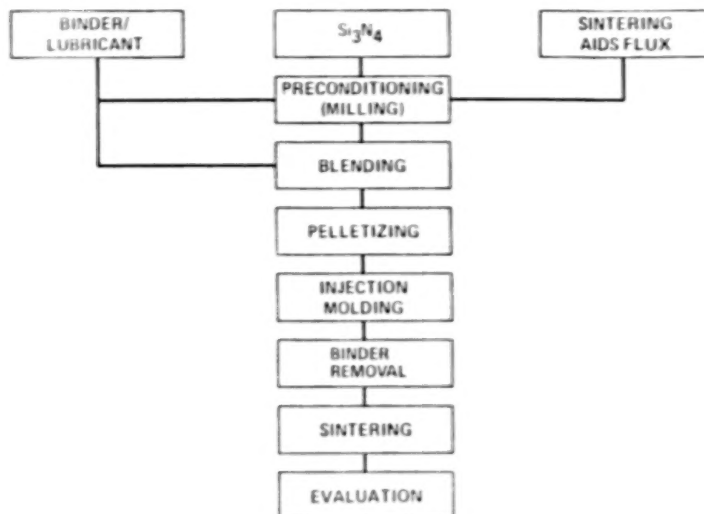
- DEVELOP FABRICATION TECHNOLOGY BASE
- INCREASE THE AS PROCESSED TEST BAR STRENGTH BY 20% (RT THRU 2550°F)
- INCREASE WEIBULL MODULUS BY 100%
- ACHIEVE INJECTION MOLDING CAPABILITY FOR LARGE COMPONENTS

NASA WORK STATEMENT: SCHEDULE AND EFFORT

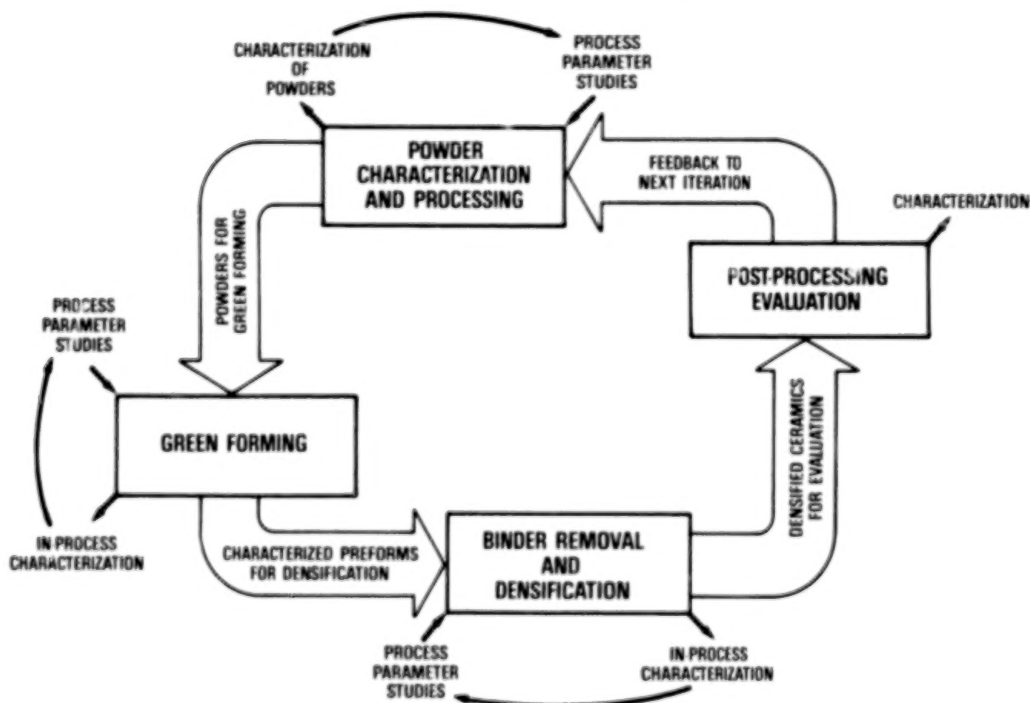
TASK NO.	DESCRIPTION	PERCENT EFFORT	YEARS FROM CONTRACT INITIATION				
			1	2	3	4	5
			← PHASE I →			← PHASE II →	
I.	BASLINE CHARACTERIZATION	5	■				
II.	MOR MATRIX	25		■	■		
III.	OPTIMIZED MOR	5			■		
IV.	BASLINE LARGE SHAPE	10			■	■	
V.	LARGE SHAPE MATRIX	25				■	■
VI.	OPTIMIZED LARGE SHAPE	10					■
VII.	MATERIAL/PROCESS IMPROVEMENT	15	■	■	■	■	■
VIII.	REPORTS/PROJECT MANAGEMENT	5	■	■	■	■	■

SPA 8506-74A

INJECTION MOLDING PROCESS



ITERATIVE APPROACH FOR IMPROVING CERAMIC MATERIAL PROPERTIES AND PROCESS CONTROLS



SMA 87775

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PROCESSING VARIABLES

STARTING POWDER

- ALTERNATE Si_3N_4
- ALTERNATE ADDITIVES
- LOT VARIATIONS

COMPOSITION

- % Al_2O_3 , Y_2O_3
- ZrO_2
- Y_2O_3 SiO_2

POWDER PROCESSING

- ALTERNATE MILLING
- CLASSIFICATION
- ELUTRIATION WASHING
- MILLING AIDS
- TIME

TOOLING

- GATE SIZE
- GATE ORIENTATION
- SEPARATION DESIGN
- TEST BARS PER SHOT

ADDITIVES

- ALTERNATE BINDERS
- % BINDER
- PLASTICIZER
- WETTING AGENT
- LUBRICANT
- DISPERSANT
- A/D BASE CONTROL

MIXING

- MIXER
- TIME
- TEMPERATURE
- SHEAR RATE
- SOLVENT
- VACUUM

INJECTION MOLDING

- MACHINE
- TEMPERATURES
- PRESSURE
- RAM SPEED
- VACUUM

DEWAX

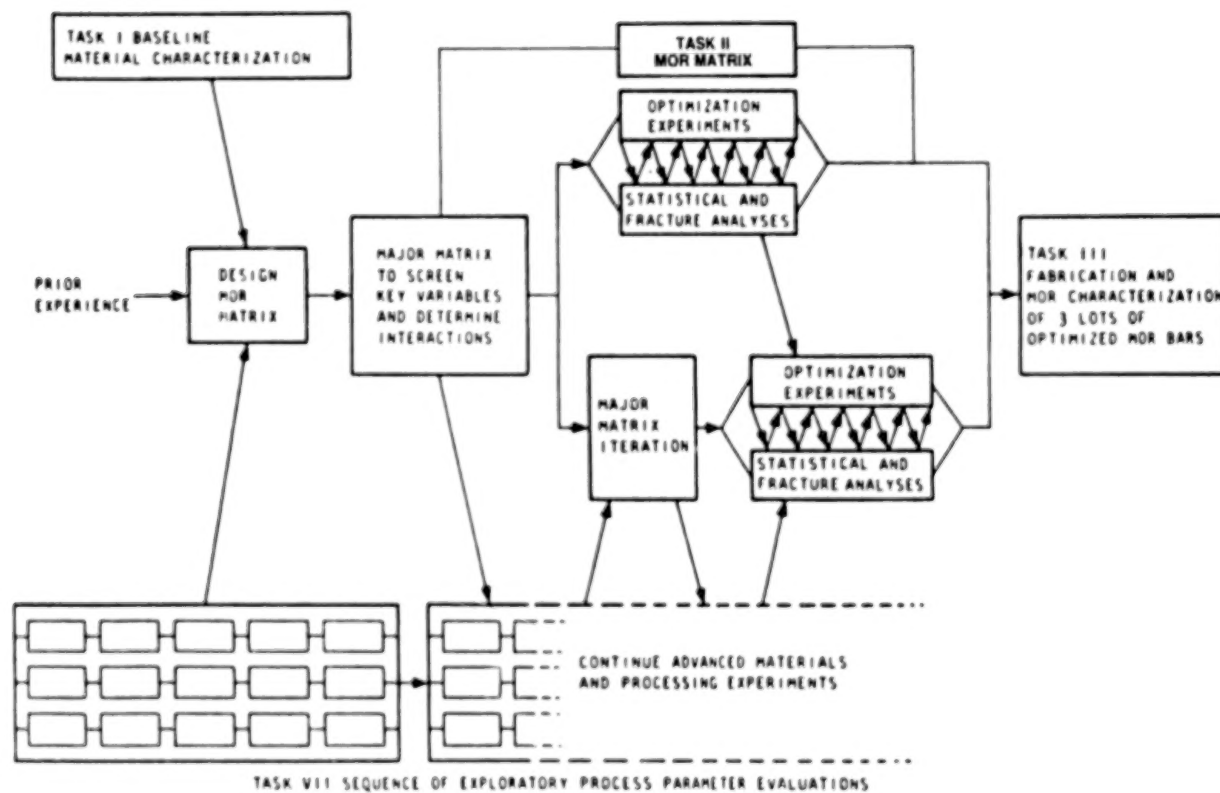
- TEMPERATURE
- PRESSURE
- CYCLE
- APPROACH
- TIME
- EQUIPMENT
- CYCLE

SINTERING

- TIME
- TEMPERATURE
- OVERPRESSURE
- CYCLE
- EQUIPMENT
- FIXTURING

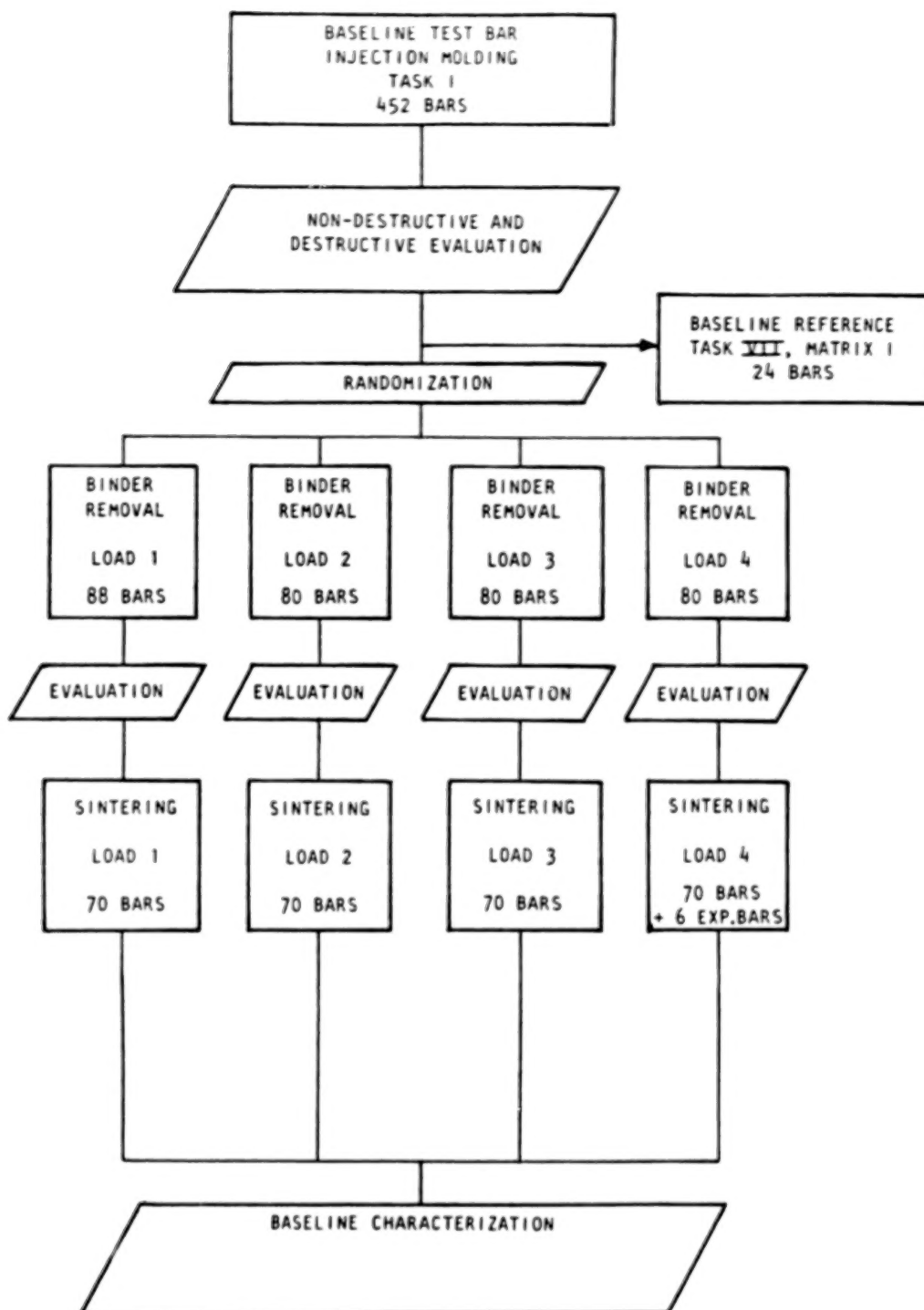
SPA 8506 197A

PHASE I DIRECTED TOWARDS TEST BARS



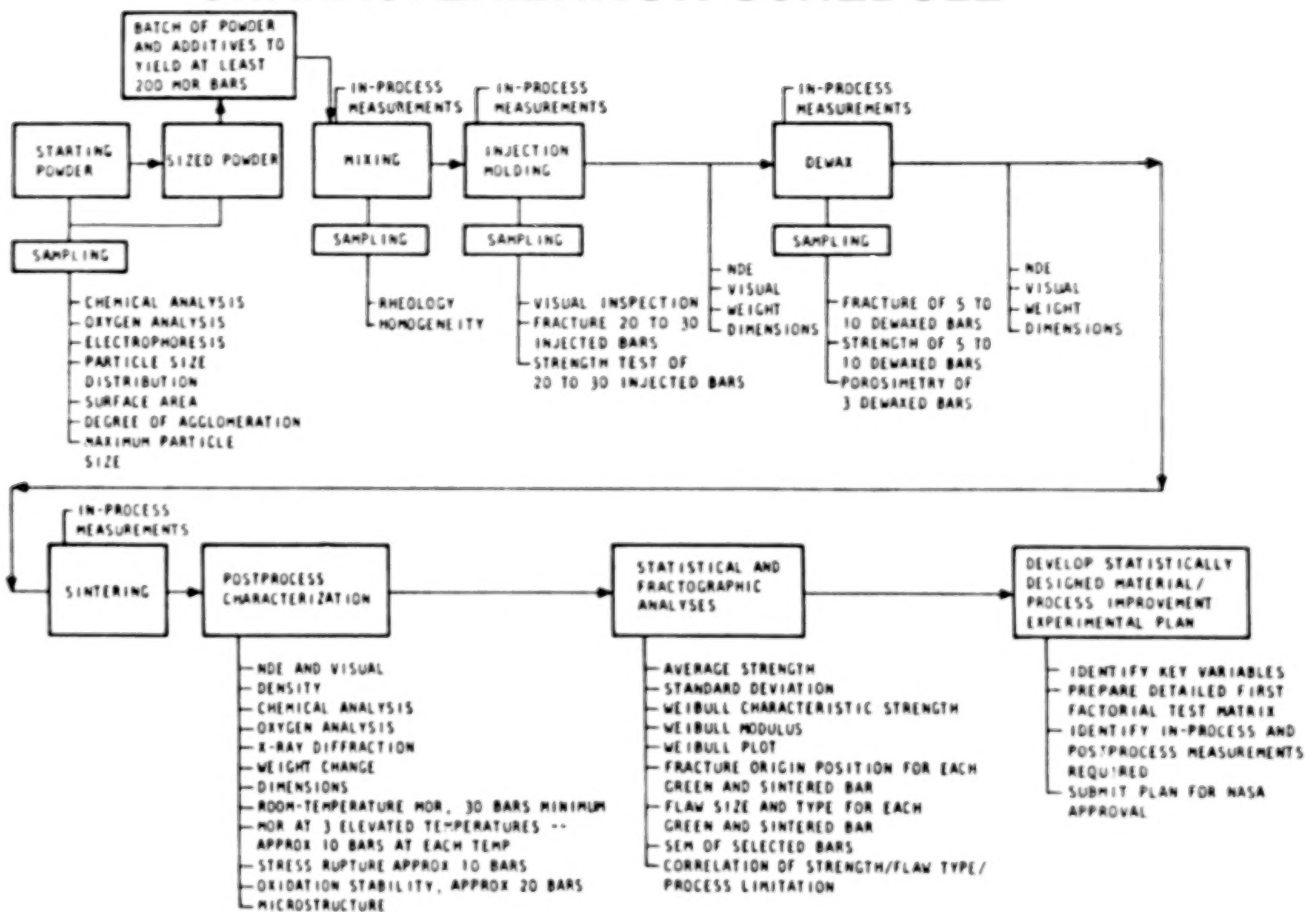
SPA 8506 79C

NASA IMPROVED Si_3N_4



SPA 85974B

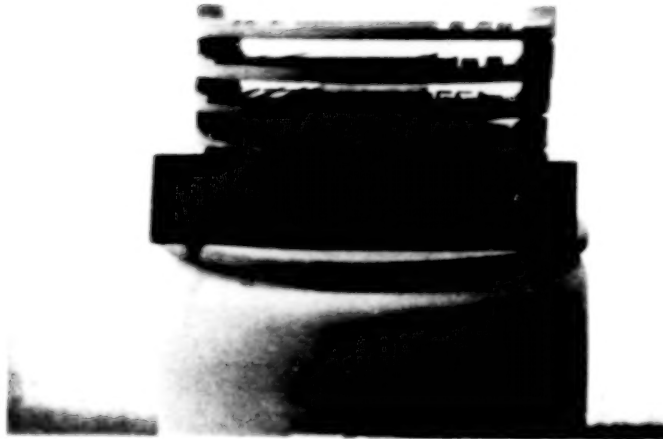
NASA IMPROVED Si_3N_4 TASK I PROCESS FLOW CHART AND CHARACTERIZATION SCHEDULE



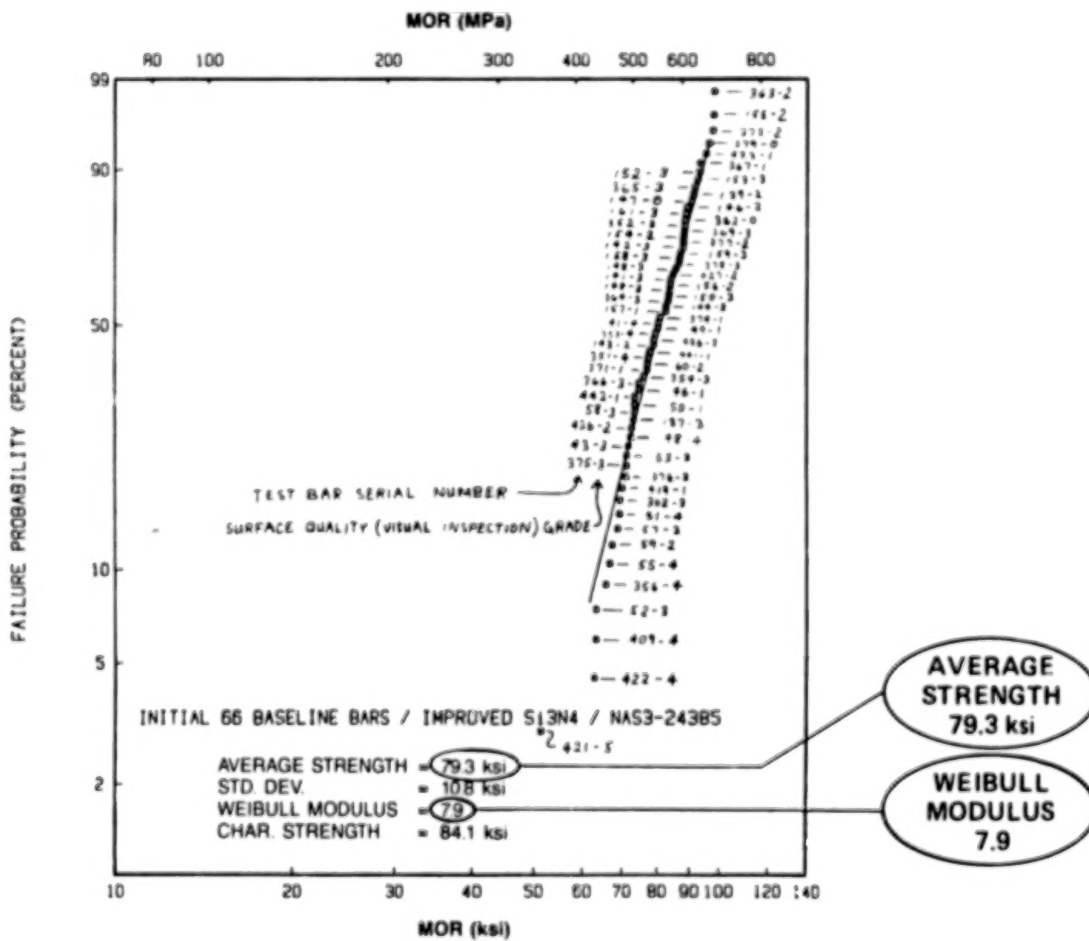
SPA 8596-80A

TEST BAR SINTERING SUPPORT

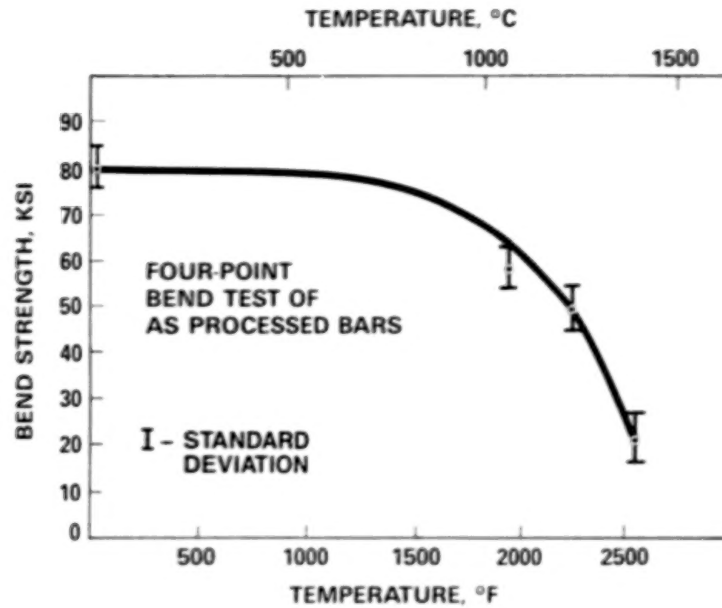
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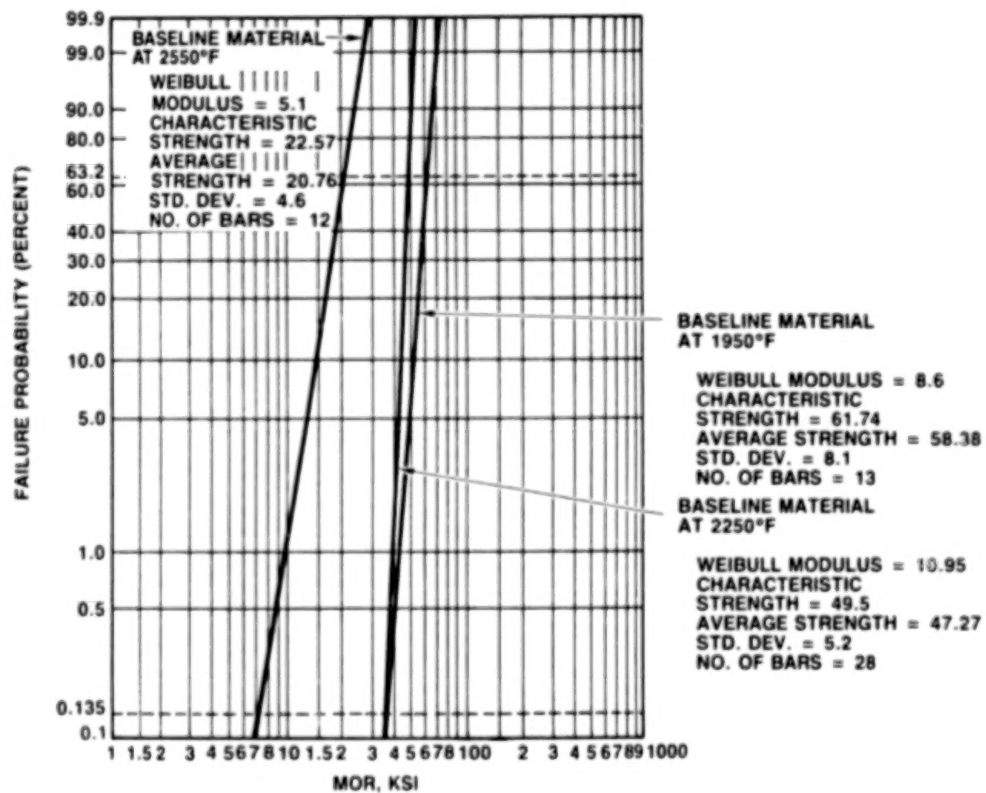
WEIBULL ANALYSIS OF BASELINE ROOM TEMPERATURE DATA



BASELINE STRENGTH



WEIBULL DISTRIBUTION FOR HIGH TEMPERATURE DATA



SPA 8794 10A

BASELINE STRESS RUPTURE

PRELIMINARY TEST CONDITIONS

1800°F	2200°F	2500°F
10 KSI — 24 HR	10 KSI — 24 HR	10 KSI — 9 HR, 42 MIN
20 KSI — 24 HR	20 KSI — 24 HR	
30 KSI — 24 HR	30 KSI — 24 HR	
40 KSI — 1 MIN	40 KSI — 24 HR	
	50 KSI — 0	

FINAL TEST RESULTS

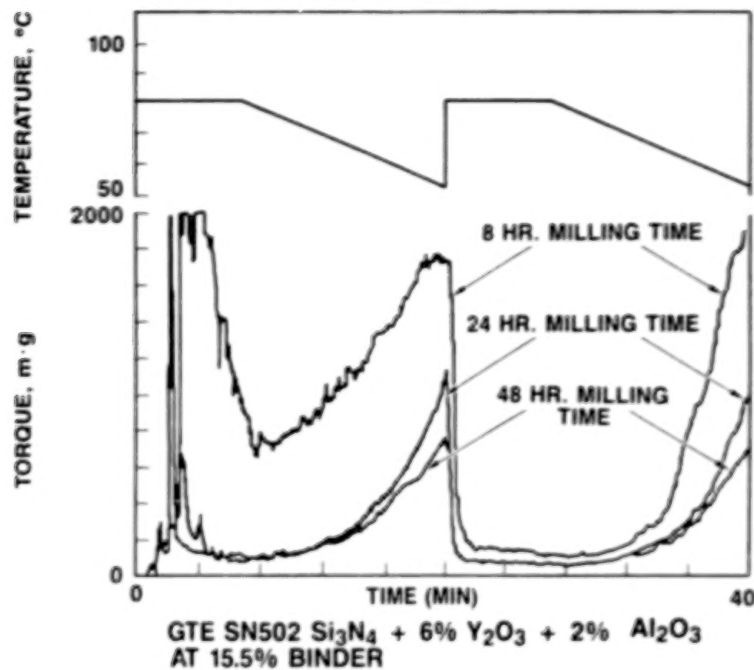
40 KSI — 7 HR, 22 MIN	40 KSI — 0	
40 KSI — 17 HR, 19 MIN	30 KSI — 1 MIN	
30 KSI — 100 HR (SURVIVED)	30 KSI — 3 HR, 38 MIN	
	30 KSI — 4 HR, 55 MIN	

SPA 8794.1

TASK VII EXPERIMENTAL MATRIXES

PROCESS VARIABLE	EXPERIMENTAL MATRIX NUMBER						
	1	2	3	4	5	6	7
RAW MATERIAL	X				X	X	
BINDER		X			X	X	X
BINDER EXTRACTION			X			X	X
INJECTION MOLDING			X			X	
POWDER PREPARATION (MILLING)			X		X		
COMPOSITION				X			
SINTERING	X			X		X	

MIXING BEHAVIOR COMPARISON ON TORQUE RHEOMETER



AS INJECTED TEST BAR SURFACES



A. 8 HR. MILLING
99°C (210°F) MOLDING

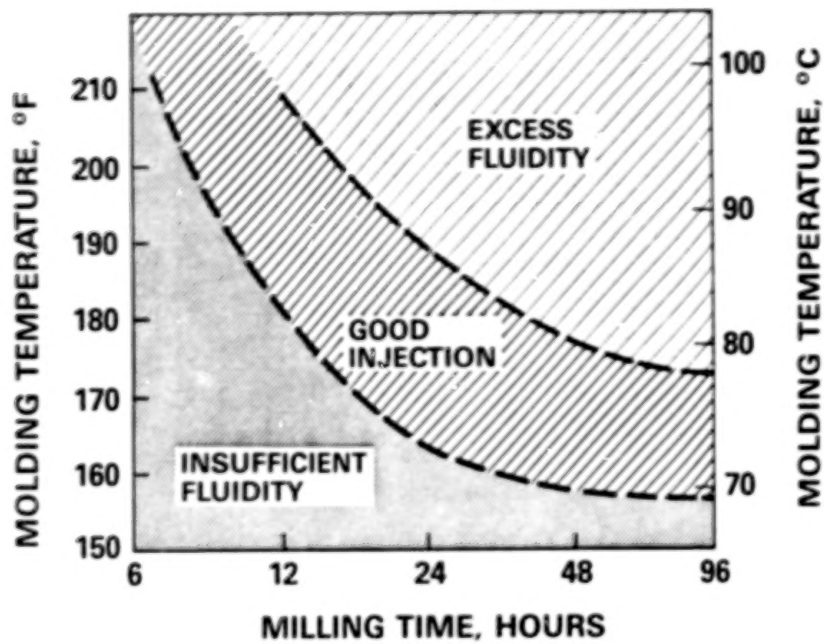
B. 8 HR. MILLING
77°C (170°F) MOLDING

C. 24 HR. MILLING
77°C (170°F) MOLDING

GTE SN502 Si_3N_4 + 6% Y_2O_3 + 2% Al_2O_3 AT 15.5% BINDER

SPA 9887-119

FLOW CHARACTERISTICS OF INJECTION MOLDING

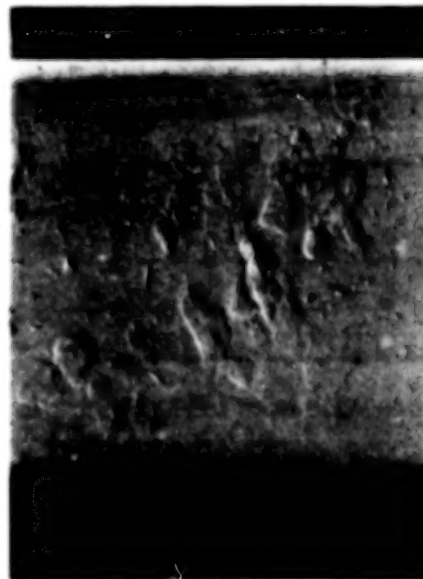


NASA IMPROVED Si_3N_4

SURFACE CHANGE DURING DEWAX — 96 HOUR MILLED POWDER

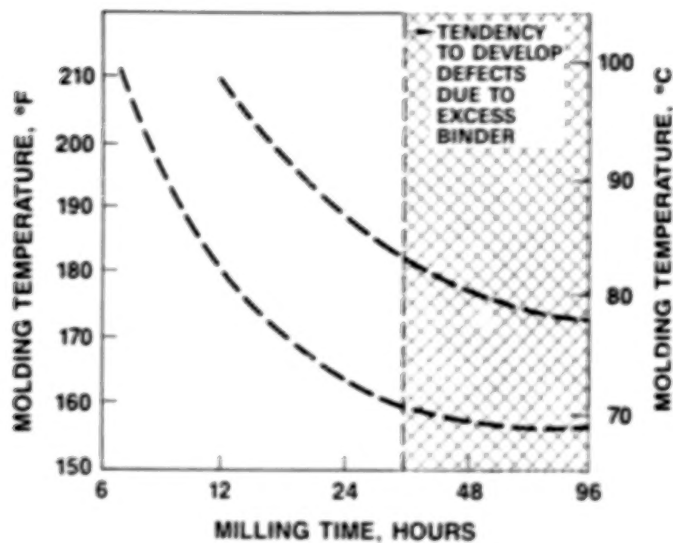


AS INJECTED



DEWAXED

DEWAX EFFECT



NASA IMPROVED Si_3N_4

TASK II EXPERIMENTAL MATRIX 1/2 REPLICATE OF A 2^5 FRACTIONAL FACTORIAL DESIGN

		C+				C-			
		D+		D-		D+		D-	
		E+	E-	E+	E-	E+	E-	E+	E-
A+	B+		abcd	abce		abde			ab
	B-	acde			ac		ad	ae	
A-	B+	bcde			bd		bd	be	
	B-		cd	ce		de			1

A = CONSOLIDATION METHODS — SINTER/HIP CYCLE (A-) VS CYCLE (A+)

B = CONSOLIDATION ENVIRONMENT — WITHOUT POWDER BED (B-) VS WITH POWDER BED (B+)

C = MIXING — SIGMA MIXER (C-) VS SIGMA MIXER PLUS EXTRUDER (C+)

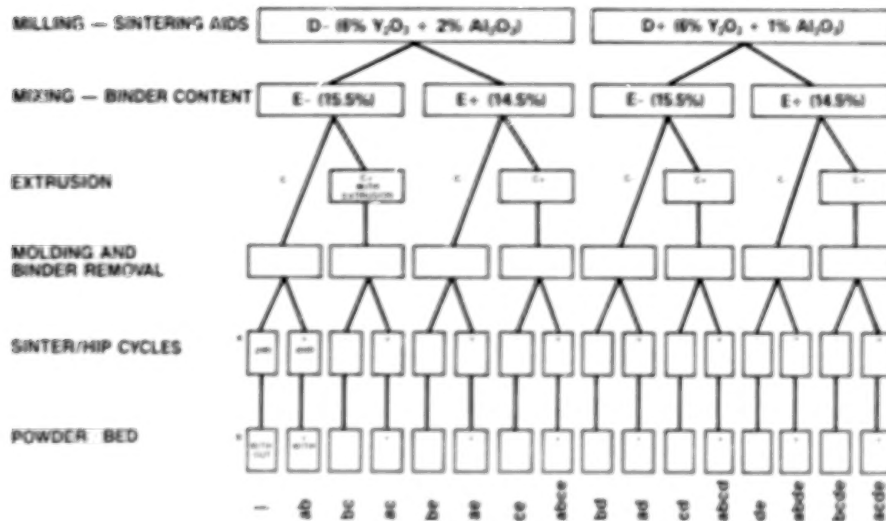
D = SINTERING AIDS — (6% Y_2O_3 + 2% Al_2O_3) (D-) VS (6% Y_2O_3 + 1% Al_2O_3) (D+)

E = BINDER CONTENT — 15.5% (E-) VS 14.5% (E+)

SPR 8802 97A

NASA IMPROVED Si_3N_4

EXPERIMENTAL MATRIX PROCESS FLOW CHART



TASK II — MOR BAR MATRIX STUDY

MONTHS 1 THROUGH 7

TASK II FIRST ITERATION SUBTASK NO.	OPERATION	1985						1986
		JUL	AUG	SEP	OCT	NOV	DEC	JAN
1	CHARACTERIZE AS-RECEIVED MATERIALS							
2	POWDER PREPARATION (SIZING)							
3	RE-EVALUATE AFTER POWDER PREPARATION							
4	BINDER ADDITION AND MIXING							
5	INJECTION HOLDING AND IN-PROCESS EVALUATION							
6	BINDER REMOVAL AND EVALUATION							
7	SINTERING AND SINTER/HIP							
8	POST-PROCESS CHARACTERIZATION							
9	STATISTICAL AND FRACTOGRAPHIC ANALYSIS							
10	DEVELOP STATISTICAL IMPROVEMENT PLAN							
11	SUBMIT TO NASA FOR GO-AHEAD PLAN FOR MONTHS 8-14							

TASK II TORQUE CHARACTERIZATION

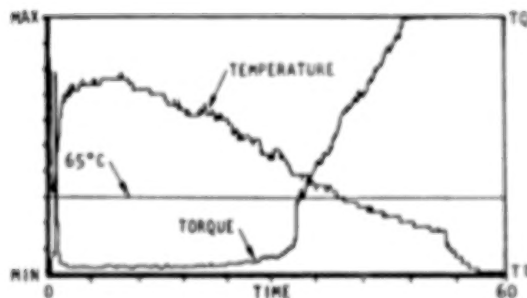
MIXING VARIATION	TORQUE AT 65°C (150°F), m·g			
	D- (6% Y_2O_3 + 2% Al_2O_3)		D+ (6% Y_2O_3 + 1% Al_2O_3)	
	E- (15.5% BINDER)	E+ (14.5% BINDER)	E- (15.5% BINDER)	E+ (14.5% BINDER)
MATRIX II-1 INJECTION MOLDING BATCHES				
C-	1450	1500	1386	1544
C+ (EXTRUDED)	1100	1452	762	1290
MATRIX II-2 INJECTION MOLDING BATCHES				
C-	876	1304	948	1175
C+ (EXTRUDED)	439	796	500	748

NOTES

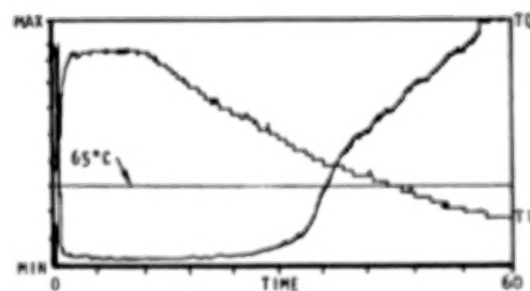
1. VALUES ARE FROM SINGLE MIXER RUNS
2. MIXER COOLING RATE WAS 1°C (1.8°F) PER MINUTE
3. m·g = meter·gram

MATRIX II-1 TORQUE CHARACTERIZATION

EFFECT OF BINDER CONTENT ON RHEOLOGY



15.5% BINDER



14.5% BINDER

MATRIX II-1 AND II-2 X-RADIOGRAPHIC YIELD

AS-INJECTED BARS

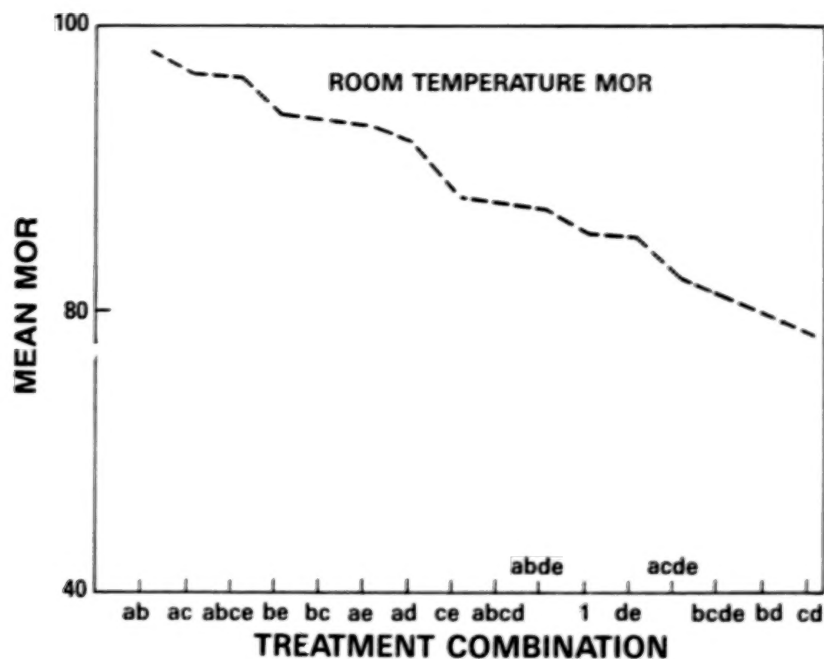
MIXING PROCEDURE	YIELD IN PERCENT			
	D- (6% Y_2O_3 + 2% Al_2O_3)		D+ (6% Y_2O_3 + 1% Al_2O_3)	
	E- (15.5% BINDER)	E+ (14.5% BINDER)	E- (15.5% BINDER)	E+ (14.5% BINDER)
	MATRIX II-1, STARCK H-1 Si_3N_4 , 200 BARS INJECTED FOR EACH CONDITION			
C-	77	77	69	76
C+ (EXTRUDED)	87	92	68	92
C- C+ (EXTRUDED)	MATRIX II-2, DENKA 9FW Si_3N_4 , 160 BARS INJECTED FOR EACH CONDITION			
	95	95	95	95
	96	96	98	96

ROOM TEMPERATURE MOR AND WEIBULL SLOPE (MATRIX II-2)

PROCESSING CONDITION	AVERAGE STRENGTH,* ksi	WEIBULL SLOPE
1	82.90	6.97
ab	97.25	13.63
bc	91.96	7.66
ac	95.58	12.73
be	92.18	10.15
ae	91.56	10.13
bd	76.20	12.84
de	82.84	7.01
ce	85.69	7.94
abce	95.28	13.44
abcd	85.02	11.24
abde	84.84	19.93
bcde	77.73	9.74
acde	78.95	5.32
ad	89.30	12.18
cd	74.40	5.64

*30 SAMPLES TESTED FOR EACH CONDITION

MATRIX II-2 MOR (DENKA 9FW)



STATISTICAL ANALYSIS

MATRIX II-2

- PROCESSING FACTORS HAVING SIGNIFICANT EFFECTS ON MOR

A, B AND D

- TWO FACTOR INTERACTIONS HAVING SIGNIFICANT EFFECTS ON MOR

B × C, B × D AND C × D

NOTE: A — SINTERED/HIP
B — POWER BED
C — MIXING
D — SINTERING AID

SINTER/HIP CYCLE EFFECT

MATRIX II-2

SINTERING/HIP 2 HRS	SINTERING/HIP 4 HRS
83.2 ksi	89.8 ksi

DIFFERENCE = 6.6 ksi

POWDER BED AND SINTERING AIDS EFFECTS

MATRIX II-2

	(B+) PB*	(B-) NO PB*
(D+) 6% Y_2O_3 + 2% Al_2O_3	81.0 Ksi	81.6 Ksi
(D-) 6% Y_2O_3 + 1% Al_2O_3	94.3 Ksi	89.1 Ksi

*PB: POWDER BED

POWDER BED AND MIXING METHOD EFFECTS

MATRIX II-2

	(B+) PB*	(B-) NO PB*
(C+) SIGMA MIXER AND EXTRUDER	87.7 Ksi	83.9 Ksi
(C-) SIGMA MIXER	87.6 Ksi	86.8 Ksi

*PB: POWDER BED

SUMMARY

- AVERAGE STRENGTH AND WEIBULL MODULUS OF BASELINE AS-PROCESSED, RANDOMLY SELECTED INJECTION MOLDED, SINTERED Si_3N_4 SAMPLES ARE 547 MPa (79.3 ksi) AND 7.9 RESPECTIVELY
- STRENGTH AND AS-PROCESSED SURFACE QUALITY ARE CLOSELY RELATED
- TORQUE RHEOMETRY HAS THE POTENTIAL TO PREDICT INJECTION MOLDING BEHAVIOR
- GOOD QUALITY AS-INJECTED BARS CAN DEGRADE DURING DEWAX IF THEY ARE PROCESSED WITH EXCESS BINDER
- FINAL TEST BAR PROPERTIES STRONGLY DEPEND ON EACH PROCESSING STEP

(CONTINUED)

N88-23882

P.9

IMPROVED PROCESSING OF Si_3N_4

William A. Sanders
NASA Lewis Research Center
Cleveland, Ohio 44135

and

George Y. Baaklini
Cleveland State University
Cleveland, Ohio 44115

CR303094

A sintered Si_3N_4 - SiO_2 - Y_2O_3 composition, NASA 6Y, was developed that reached four-point flexural average strength/standard deviation values of 857/36, 544/33, and 462/59 MPa at room temperature, 1200 and 1370 °C respectively. These strengths represented improvements of 56, 38, and 21 percent over baseline properties at the three test temperatures. At room temperature the standard deviation was reduced by more than a factor of three. These accomplishments were realized by the iterative utilization of conventional x-radiography to characterize structural (density) uniformity as affected by systematic changes in powder processing and sintering parameters. Accompanying the improvement in mechanical properties was a change in the type of flaw causing failure from a pore to a large columnar β - Si_3N_4 grain typically 40-80 μm long, 10-30 μm wide, and with an aspect ratio of 5:1.

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117, 118

IMPROVED PROCESSING OF Si_3N_4

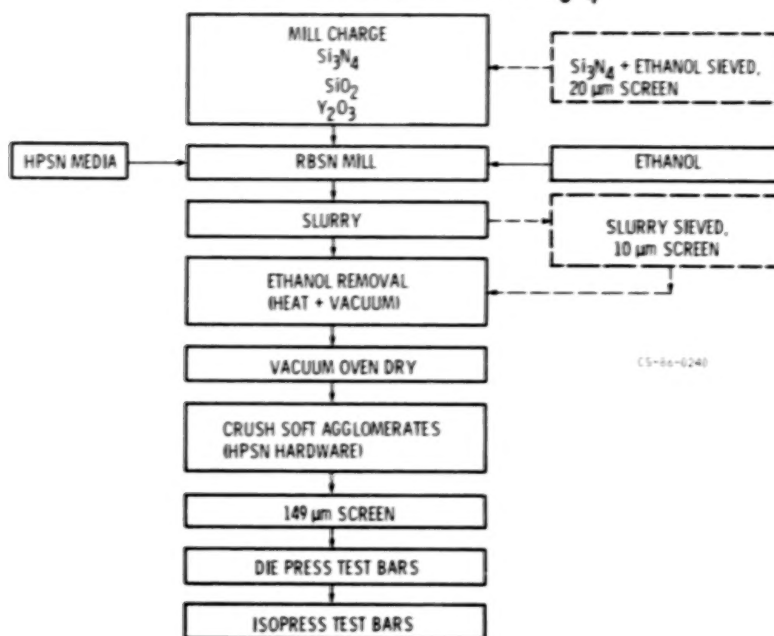
OBJECTIVE

TO IMPROVE THE STRENGTH AND UNIFORMITY OF SINTERED SILICON NITRIDE BY A SYSTEMATIC INVESTIGATION OF POWDER PROCESSING AND SINTERING VARIABLES AS THEY AFFECT RADIO GRAPHICALLY CHARACTERIZED DENSITY GRADIENTS, AND CONSEQUENTLY THE STRENGTH LEVEL AND SCATTER OF SILICON NITRIDE

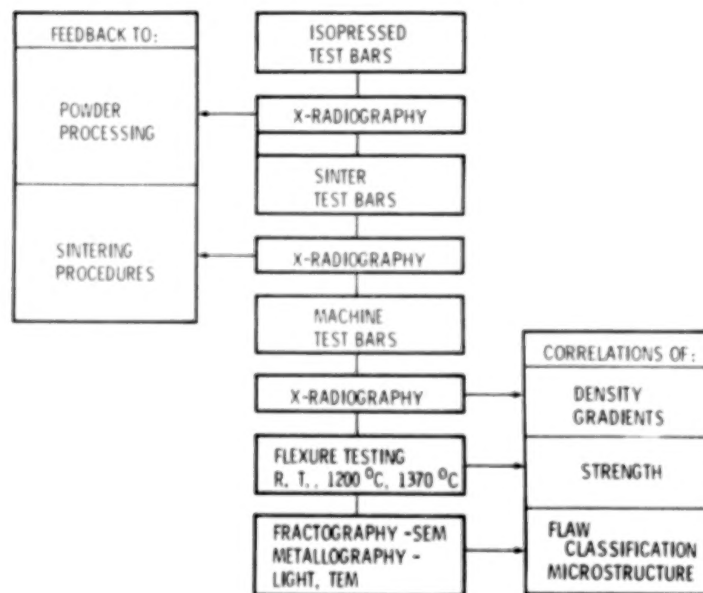
CHARACTERIZATION OF SILICON NITRIDE AND OXIDE POWDERS

MATERIAL	SOURCE	MANUFACTURERS DESIGNATION	PURITY, %	SPECIFIC SURFACE AREA, $\text{m}^2 \cdot \text{g}^{-1}$	X-RAY DIFFRACTION ANALYSIS, %			CHEMICAL ANALYSIS		
					α	β	FREE Si	OXYGEN, wt %	CARBON, wt %	SPECTROGRAPHIC ANALYSIS, ppm
Si_3N_4	KBI-AME	HIGH PURITY	99.5	4.7	83.7	15.7	0.6	0.89	0.18	240Al, 60Ca, 20Co, 50Cr, 1280Fe, 20Mg, 30Mn, 40Ti, 40V, 590Y, 30Zn, 10Zr
SiO_2	APACHE CHEMICALS	6846	99.99	166	----	----	---	----	.16	220Al, 150Ca, 30Cr, 50Cu, 50Fe, 130Mg, 90Mn, 340Na, 40Ti
Y_2O_3	MOLYCORP	5600	99.9	7.5	----	----	---	---	.11	60Cu, 60Mg, 40 R.E. OXIDES

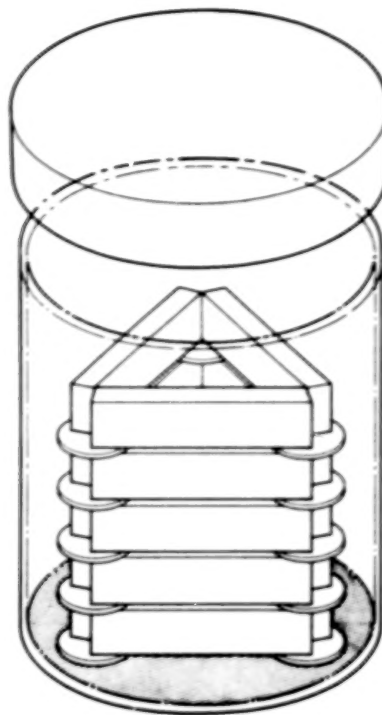
POWDER PROCESSING OF NASA 6Y Si₃N₄



EVALUATION OF NASA 6Y Si₃N₄

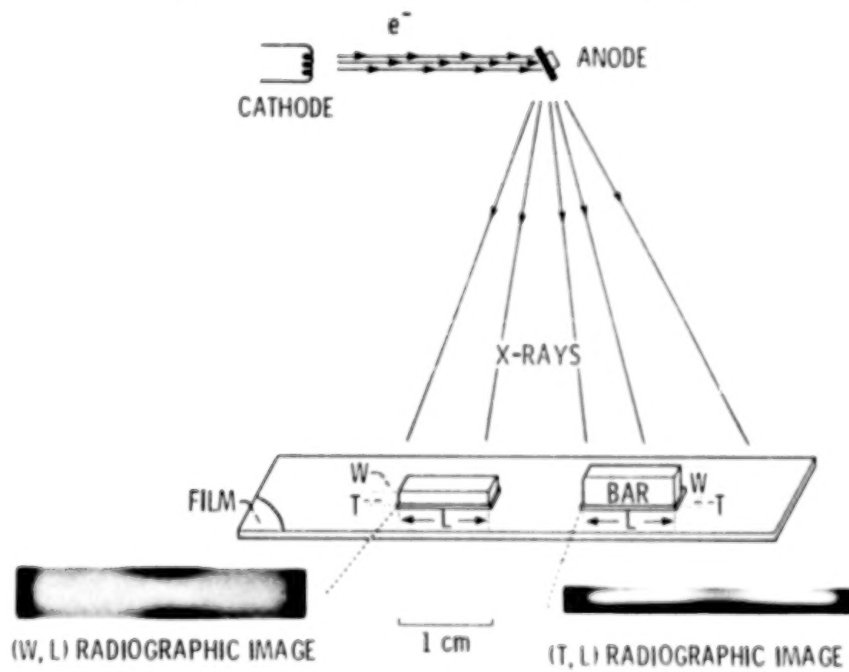


Si_3N_4 BAR/BN SETTER ARRANGEMENT IN W SINTER CUP



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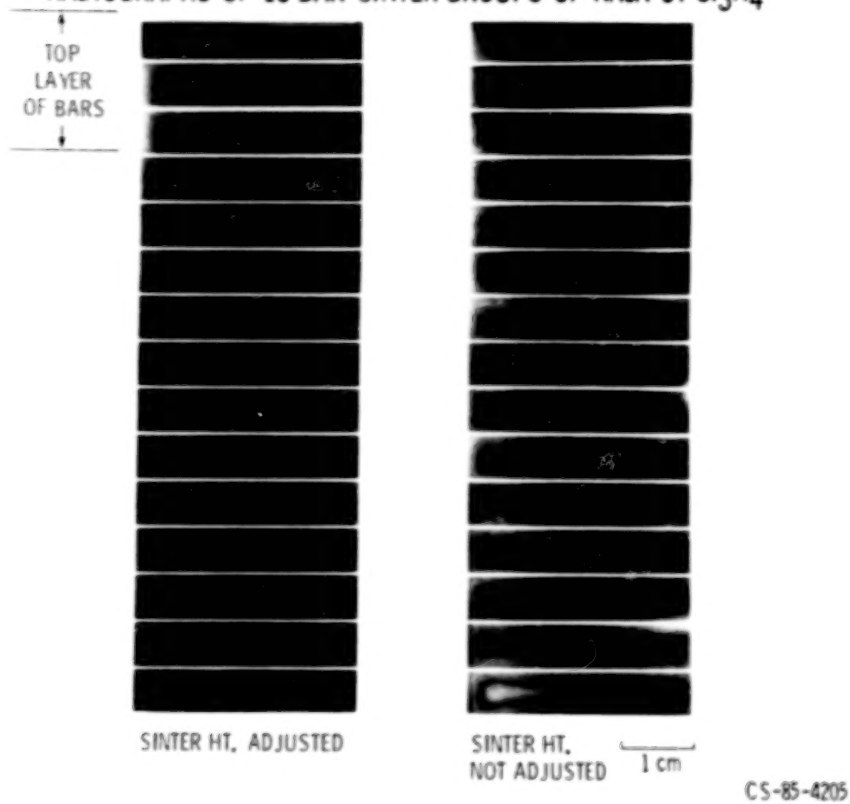
CONVENTIONAL RADIOGRAPHY OF NASA 6Y Si_3N_4 TEST BARS



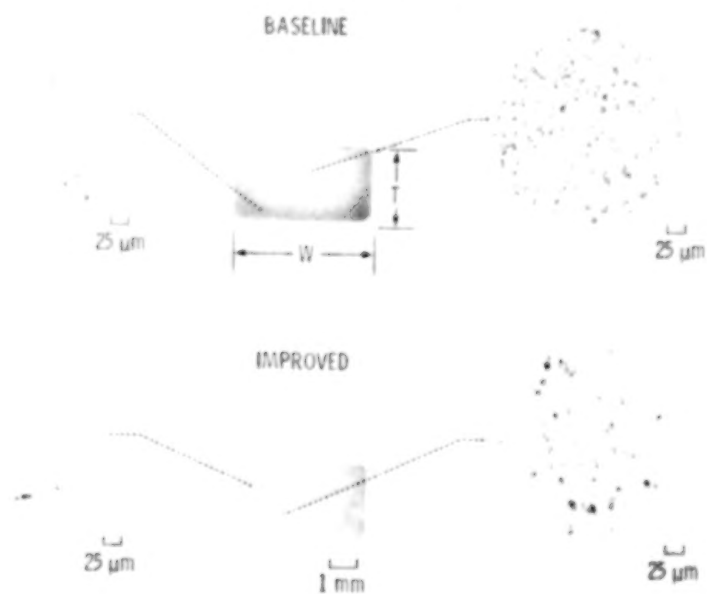
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RADIOGRAPHS OF 15-BAR SINTER-GROUPS OF NASA 6Y Si_3N_4



CASE-CORE STRUCTURE COMPARISON FOR BASELINE
AND IMPROVED NASA 6Y Si_3N_4



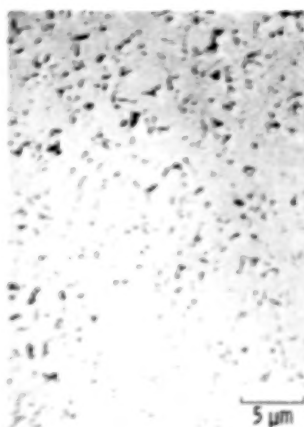
CS-85-4197

TEM MICROSTRUCTURES OF NASA 6Y Si_3N_4 EFFECT OF GRINDING TIME



$t_g = 24 \text{ hr}$

0.3 - 4.0 μm EQUIAX
0.35 - 3.5 μm COLUM. WIDTH
1:2 TO 1:6 ASPECT RATIO
70 VOL. % COLUM.



$t_g = 100 \text{ hr}$

0.2 - 3.5 μm EQUIAX
0.4 - 2.0 μm COLUM. WIDTH
1:2 TO 1:14 ASPECT RATIO
40 VOL. % COLUM.



$t_g = 300 \text{ hr}$

0.2 - 3.0 μm EQUIAX
0.25 - 2.0 μm COLUM. WIDTH
1:2 TO 1:8 ASPECT RATIO
20 VOL. % COLUM.

CS-85-4209

SINTERING CONDITIONS AND RESULTS FOR $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ COMPOSITION NASA 6Y SINTERED AT 2140 °C

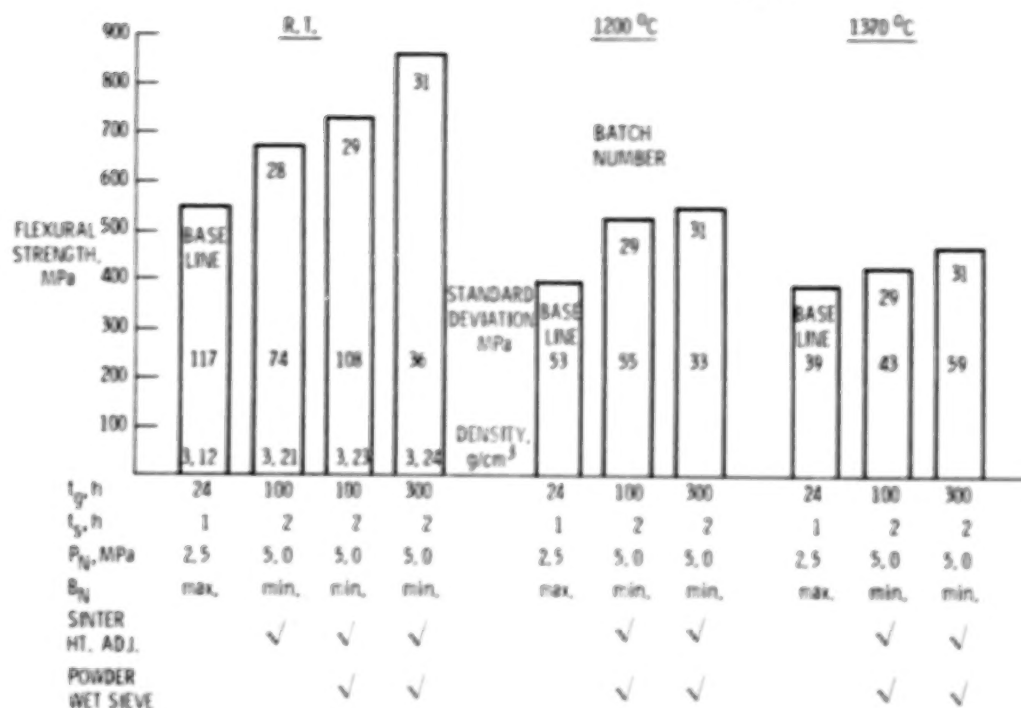
NASA 6Y BATCH NUMBER	MILLING TIME, hr	SINTERING CONDITIONS			SINTERING RESULTS ^a		
		TIME, hr	PN, MPa	BN SETTER CONTACT	AVERAGE WEIGHT LOSS, %	AVERAGE WIDTH SHRINKAGE, %	AVERAGE MACHINED DENSITY, g-cm ⁻³
BASLINE	24	1	2.5	MAX	3.85	15.6	3.12
11	100			MAX	5.14	17.6	3.23
13	100			MIN	4.93	17.6	3.24
12	300			MAX	5.74	18.0	3.25
14	300			MIN	5.42	17.5	3.24
15	24	2	5.0		5.10	17.2	3.22
16	24				4.44	16.8	3.23
17	100				4.39	17.3	3.23
20	100				2.81	17.2	3.22
25	300				4.88	17.8	3.28
28 ^b	100				3.77	17.3	3.21
29 ^{b,c}	100				3.06	16.1	3.23
31 ^{b,c}	300				3.71	17.3	3.24
21 (2050 °C)	100				1.65	14.9	3.05

^aAVERAGE FOR EACH COMPOSITION REPRESENT 30 BARS EXCEPT FOR BASELINE WHICH REPRESENTS 150 BARS AND BATCH 28 WHICH REPRESENTS 15 BARS.

^bSINTER CUP RAISED 3.8 cm.

^c Si_3N_4 POWDER WET SIEVED BEFORE AND AFTER MILLING.

COMBINED EFFECT OF MODIFIED PROCESSING/SINTERING PROCEDURES ON THE FLEXURAL STRENGTH OF NASA 6Y Si₃N₄



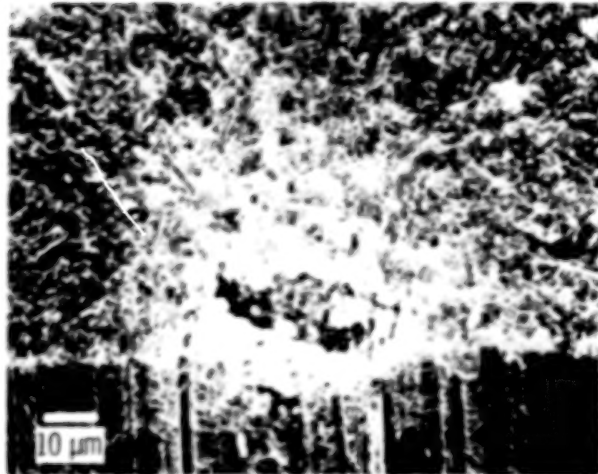
ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si₃N₄

		SUB-SURFACE PORE	SURFACE PORE	SEAM	SUB-SURFACE AGGLOMERATE	COLUMNAR GRAIN	SURFACE DEFECT	METALLIC INCLUSION
R. T. FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	56	44	28	25	17	13	9
	PERCENT OF TOTAL	29	23	14	13	9	7	5
1200 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	23	19	9	7	14	0	18
	PERCENT OF TOTAL	26	21	10	8	15	0	20
1370 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	30	15	25	3	32	0	22
	PERCENT OF TOTAL	24	12	20	2	25	0	17

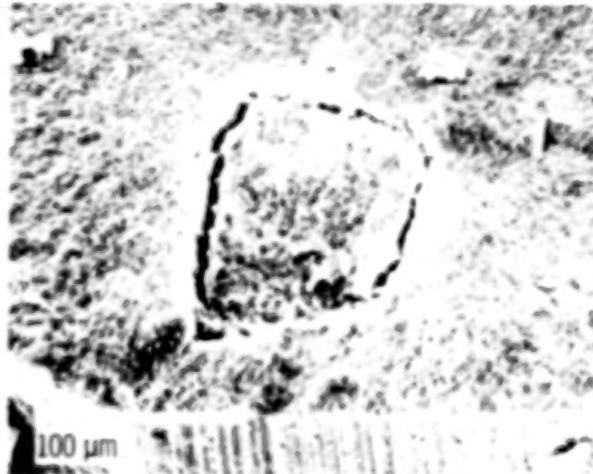
^aNUMBER EXCLUDES 111, 47, AND 41 BARS FOR R. T., 1200 °C, AND 1370 °C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.

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CRITICAL FLAWS IN R. T. FRACTURE OF NASA 6Y Si_3N_4



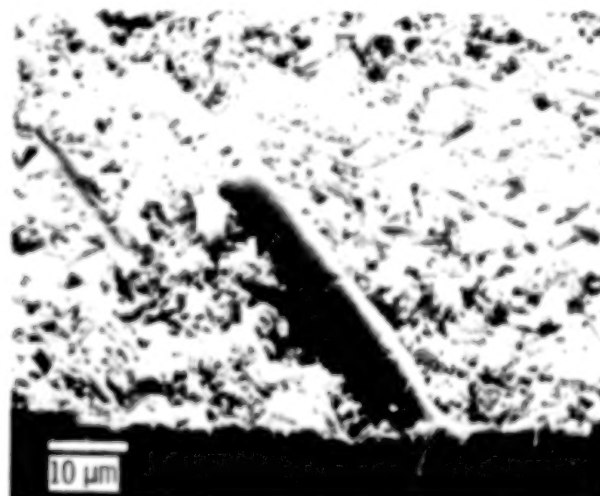
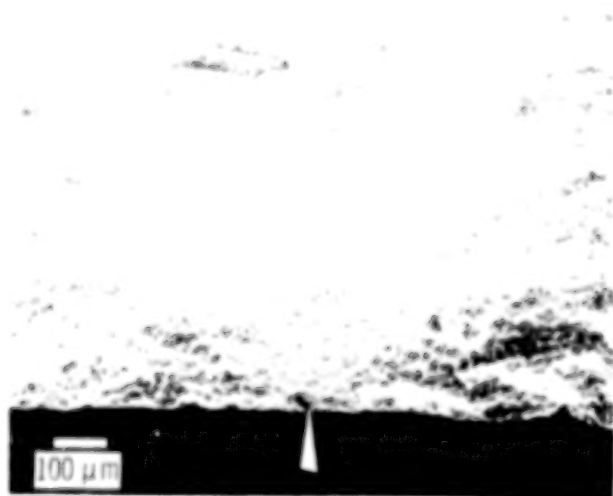
SURFACE PORE, $\sigma_f = 620$ MPa



AGGLOMERATE, $\sigma_f = 470$ MPa

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COLUMNAR Si_3N_4 GRAIN CRITICAL FLAW IN R. T. FRACTURE OF IMPROVED NASA 6Y Si_3N_4

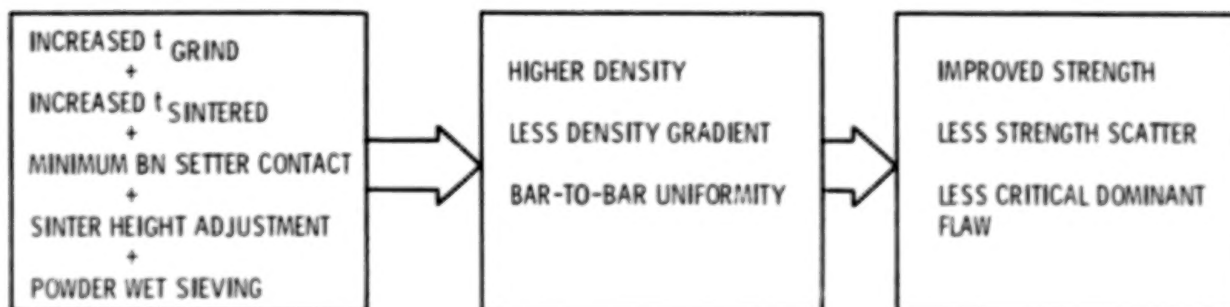


$\sigma_f = 905$ MPa

CS-85-4201

SUMMARY

APPLICATION OF CONVENTIONAL RADIOGRAPHY VERY BENEFICIAL IN GUIDING POWDER
PROCESSING AND SINTERING PARAMETER CHANGES FOR IMPROVED Si_3N_4



D11-
P10

N88-23883

COLLOIDAL CHARACTERIZATION OF
SILICON NITRIDE AND SILICON CARBIDE*

Donald L. Feke
Case Western Reserve University CH 724
Cleveland, Ohio 44106

The colloidal behavior of aqueous ceramic slips strongly affects the forming and sintering behavior and the ultimate mechanical strength of the final ceramic product. The colloidal behavior of these materials, which is dominated by electrical interactions between the particles, is complex due to the strong interaction of the solids with the processing fluids. A surface titration methodology, modified to account for this interaction, has been developed and used to provide fundamental insights into the interfacial chemistry of these systems. Various powder pretreatment strategies were explored to differentiate between true surface chemistry and artifacts due to exposure history. The colloidal behavior of both silicon nitride and carbide is dominated by silanol groups on the powder surfaces. However, the colloid chemistry of silicon nitride is apparently influenced by an additional amine group. With the proper powder treatments, silicon nitride and carbide powder can be made to appear colloidally equivalent. The impact of these results on processing control will be discussed.

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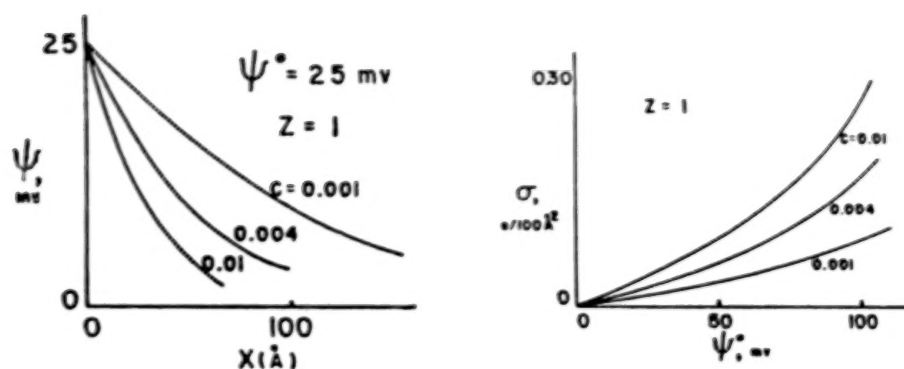
*Work done under NASA Grant NAG3-468.

WHY?

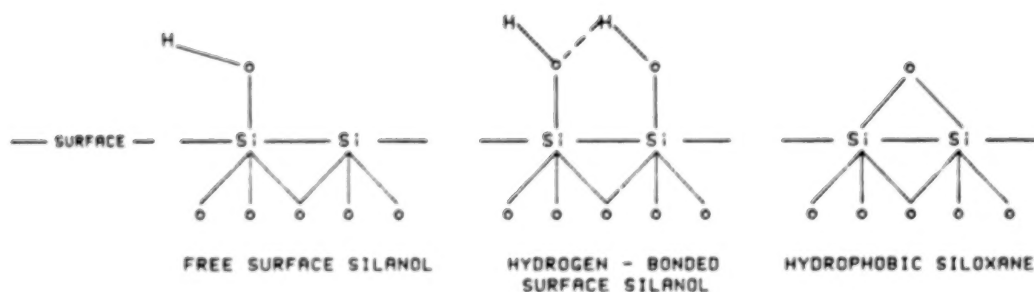
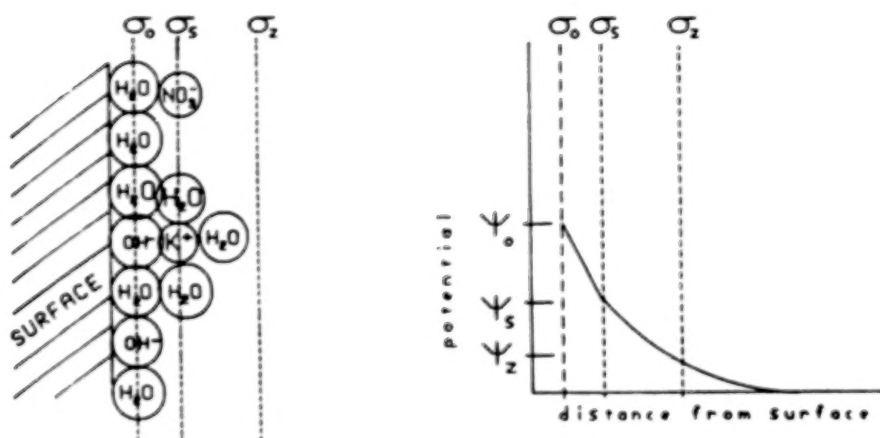
- * SINTERING OF COVALENT SOLIDS
REQUIRES SUBMICRON PARTICLES
(PROCESSING COLLOIDAL DISPERSIONS)
 - CERAMIC POWDERS ACQUIRE
SURFACE CHARGE AND INTERACT
WITH IONS IN PROCESSING FLUID
 - STABILITY AND RHEOLOGY
DOMINATED BY ELECTROSTATIC
EFFECTS
- * STRONG CORRELATION BETWEEN
DISPERSION QUALITY AND FINAL
PROPERTIES OF SINTERED CERAMIC

- TECHNIQUES - SPECTROSCOPIC CHARACTERIZATION
FTIR, ESCA, SIMS, AUGER
- ELECTROPHORETIC CHARACTERIZATION
ZETA POTENTIAL
 - TITRATION OF SURFACE GROUPS
SURFACE CHARGE
 - RHEOLOGICAL CHARACTERISTICS
VISCOMETRY
 - STABILITY CHARACTERIZATION
SEDIMENTATION

RELATIONSHIP BETWEEN SURFACE POTENTIAL AND SURFACE CHARGE



DEVELOPMENT OF SURFACE CHARGE AND SURFACE POTENTIAL



ADSORPTION OF POTENTIAL DETERMINING IONS:



ORIGIN OF SURFACE POTENTIAL

REVERSIBLE ELECTRODE --

NERNST EQUATION RELATES SURFACE POTENTIAL (Ψ)
TO CONCENTRATION OF POTENTIAL DETERMINING IONS:

$$\Psi = \frac{2.303RT}{ZF} \text{LOG}(C/C_{2P})$$

AMPHOTERIC OXIDE --

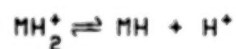
ASSUMING H^+ AND OH^- ARE POTENTIAL DETERMINING
AND EXHIBIT NERNSTIAN BEHAVIOR:

$$\Psi = 59.7(pH_{PZC} - pH)$$

ORIGIN OF SURFACE SPECIES --

THERMODYNAMICS OF THE DOUBLE LAYER

SITE MODEL OF SOLID/LIQUID INTERFACE:



EQUATE CHEMICAL POTENTIALS:

BULK COMPONENTS--

$$\mu_j = \mu_j^0 + RT \ln a_j$$

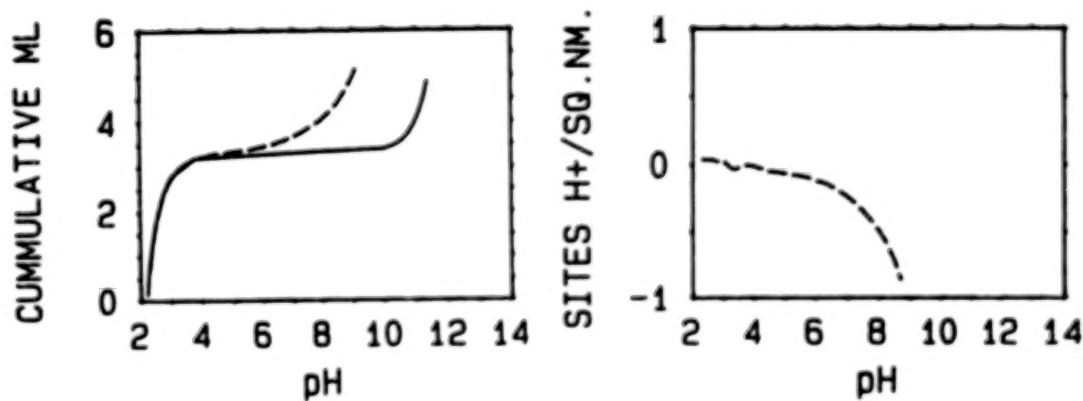
SURFACE SITES--

$$\mu_{H_j} = \mu_{H_j}^0 + RT \ln a_{H_j} + ZF\psi$$

EXPERIMENTAL APPROACH

- IDENTIFY PRETREATMENT METHOD TO YIELD REPRODUCIBLE, PRISTINE SURFACE
- INVESTIGATE EFFECT OF MANUFACTURING HISTORY, SUBSTRATE ON ADSORPTION
- COMPARE SILICON NITRIDE, SILICON CARBIDE AND SILICA
- EXPLORE THE ROLE OF ELECTROLYTE
- COMPARE TITRATION RESULTS WITH RESULTS FROM OTHER METHODS

POTENTIOMETRIC TITRATION



FOR AMPHOTERIC COLLOID:

$$\sigma_s = F (\Gamma_{H^+} - \Gamma_{OH^-})$$

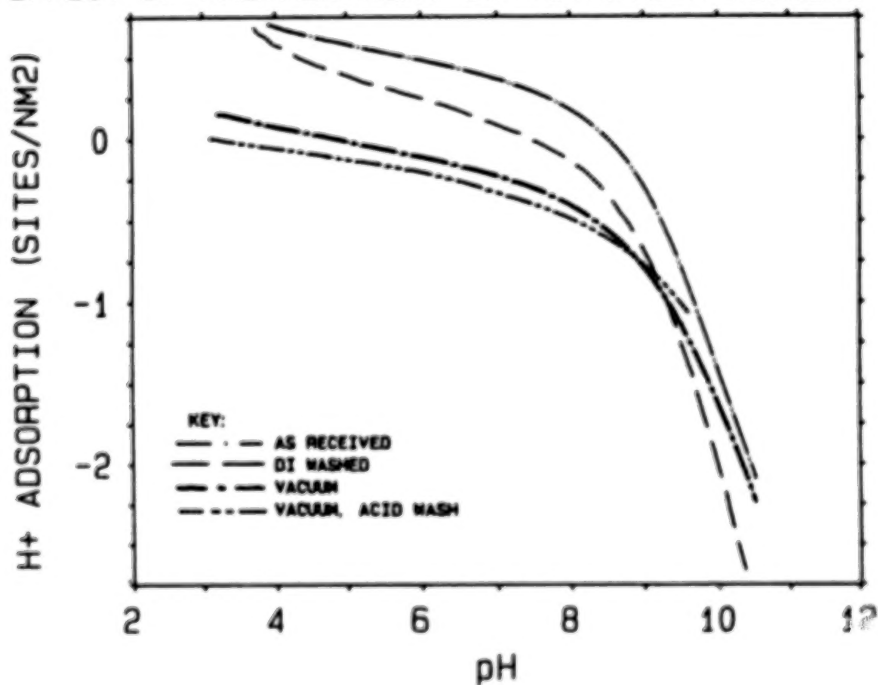
WHERE F = FARADAY'S CONSTANT

$\Gamma_{H^+}, \Gamma_{OH^-}$ = EQUIVALENTS OF H⁺ OR OH⁻ BOUND TO SURFACE

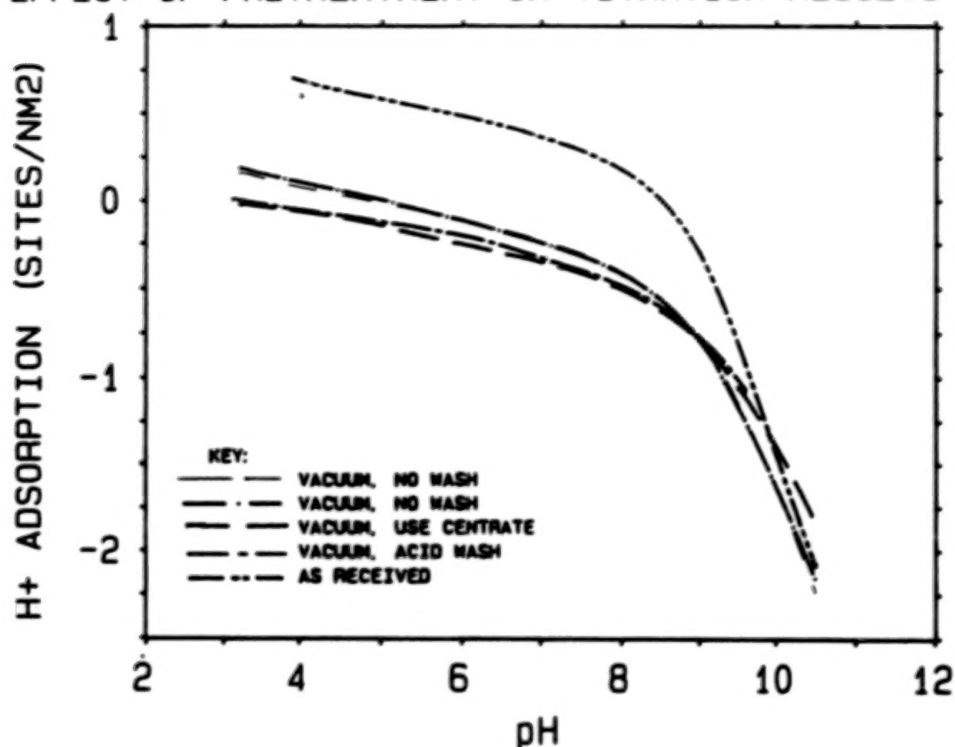
HANDLING AND PRETREATMENT:

- * NONE (AS RECEIVED)
- * FIRE 500°C IN ARGON
- * FIRE 300°C IN OXYGEN
- * WASH IN DI WATER, THEN:
 - NO DRY
 - DRY, MILD CONDITIONS
 - DRY RAPIDLY
- * WASH IN ACIDIC ELECTROLYTE
- * EXPOSE TO MODERATE VACUUM

EFFECT OF PRETREATMENT ON TITRATION RESULTS



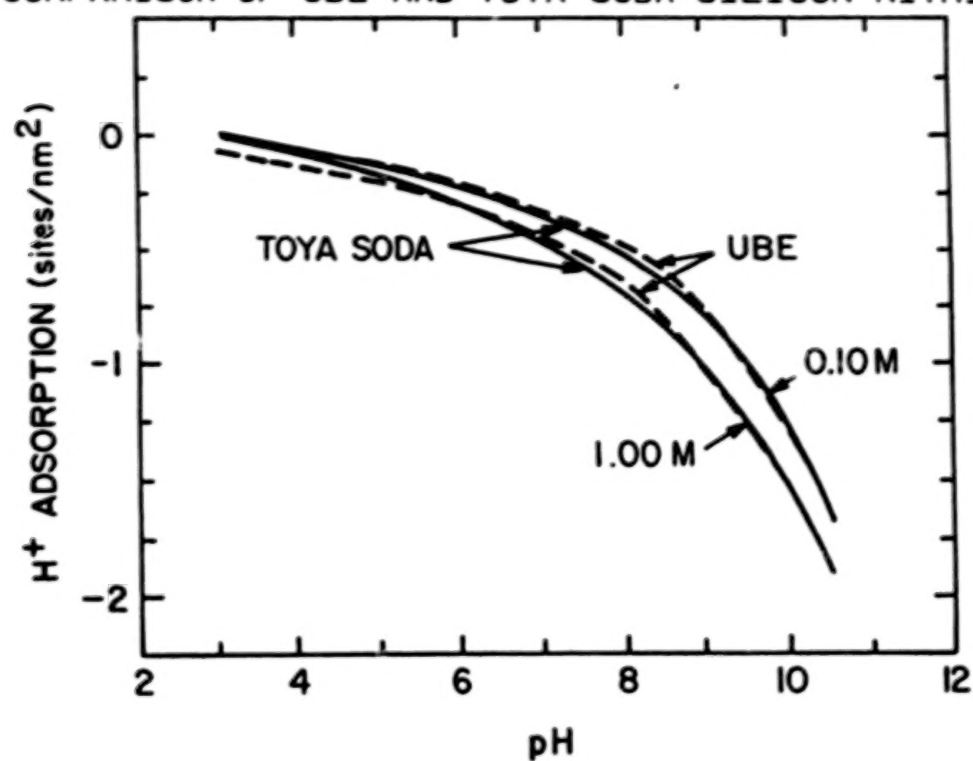
EFFECT OF PRETREATMENT ON TITRATION RESULTS



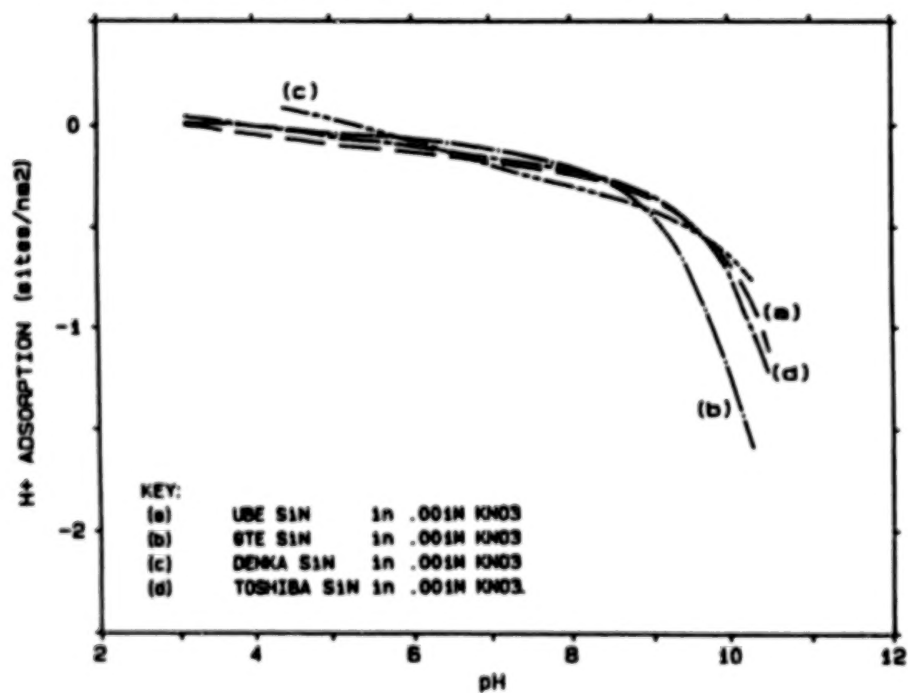
SUMMARY OF RESULTS

- * PHYSISORBED SPECIES REMOVED
 - BAKE IN DRY ENVIRONMENT
 - EXPOSE TO MODERATE VACUUM
- * CHEMISORBED SPECIES DESORB RAPIDLY
IN ACIDIC ELECTROLYTE
- * SILICON NITRIDE REACTS WITH AQUEOUS
SOLUTION TO RE-FORM ORIGINAL ADSORBED
SPECIES
- * WASHING IN ACIDIFIED SOLUTION REMOVES
ALL ADSORBATE, BUT LEAVES SURFACE
UNALTERED FROM "AS RECEIVED" STATE

COMPARISON OF UBE AND TOYA SODA SILICON NITRIDE

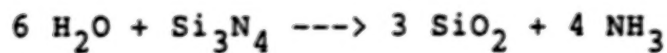


COMPARISON OF SILICON NITRIDE FROM FOUR MANUFACTURERS

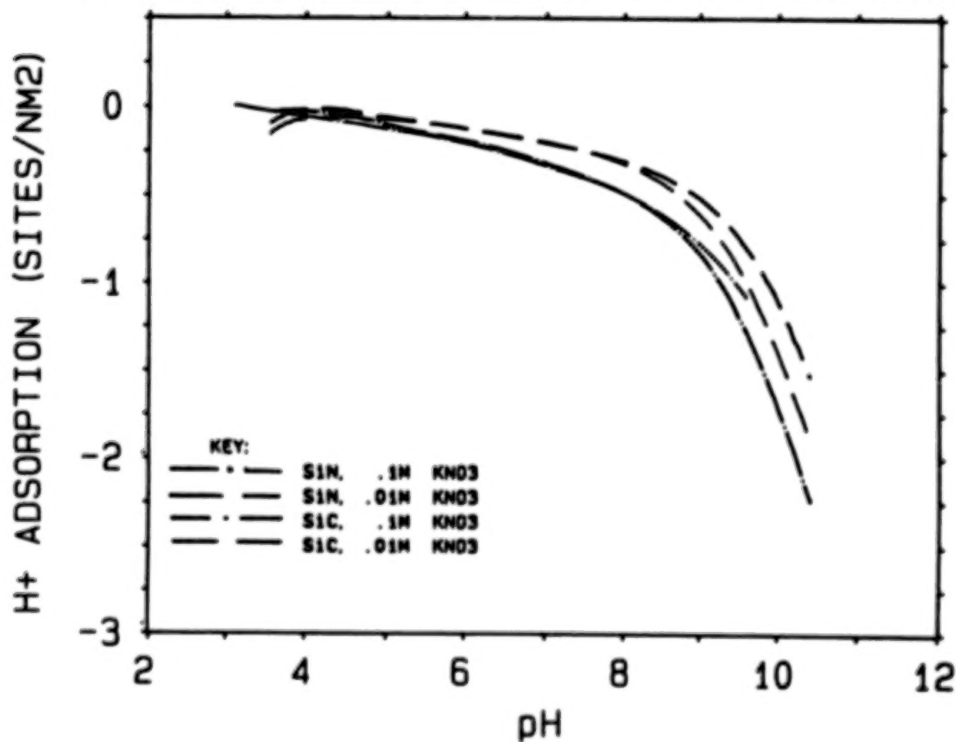


HYPOTHESES

- * TITRATABLE SURFACE SPECIES IS SILICA
- * SPECIES ADSORBED ON SILICON NITRIDE IS AMMONIA
 - MOST PHYSORBED, SOME CHEMISORBED
 - SIMILAR TO REPORTED ADSORPTION OF AMMONIA ON SILICA
- * AMMONIA IS FORMED BY HYDROLYSIS OF SILICON NITRIDE:



COMPARISON OF SILICON NITRIDE AND SILICON CARBIDE



SUMMARY OF SURFACE TITRATION DATA

- * SUGGEST PZC < pH 3 FOR BOTH SILICA AND SILICON CARBIDE
- * SUGGEST PZC > pH 6 FOR MOST SILICON NITRIDES
- * LITTLE DIFFERENCE AMONG VARIOUS MANUFACTURERS OF SILICON NITRIDE
- * LITTLE DIFFERENCE BETWEEN SILICON NITRIDE AND SILICON CARBIDE Si-OH SITE DENSITY
- * WITH CAREFUL PRETREATMENT, DATA IS REPRESENTATIVE OF NATIVE SURFACE AND IS REPRODUCIBLE

N88-23884¹²⁷

NDE OF STRUCTURAL CERAMICS BY PHOTOACOUSTIC MICROSCOPY

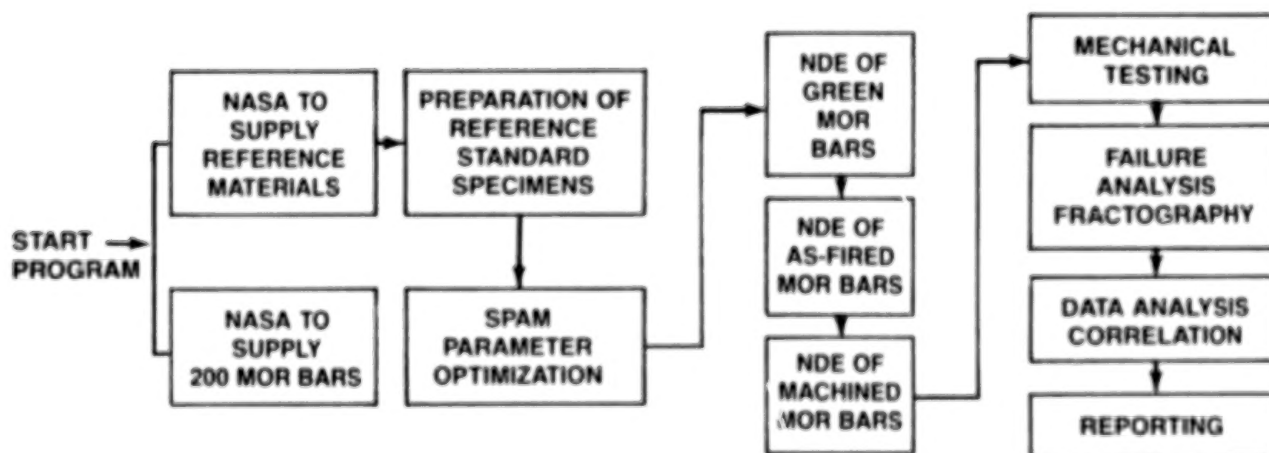
P.K. Khandelwal
Allison Gas Turbine Division
General Motors Corporation
P.O. Box 420, Speed Code W-5
Indianapolis, Indiana 46206-0420

Photoacoustic microscopy (PAM) has been utilized to detect surface and subsurface defects in structural ceramic materials. A computerized PAM data acquisition, color imaging and analysis system has been developed and used under this program. Sub-surface simulated cylindrical holes can be detected to about 1 mm below the interrogating surface. Simulated tight surface cracks of 96 μm length and 48 μm depth can be detected in these materials under optimum conditions.

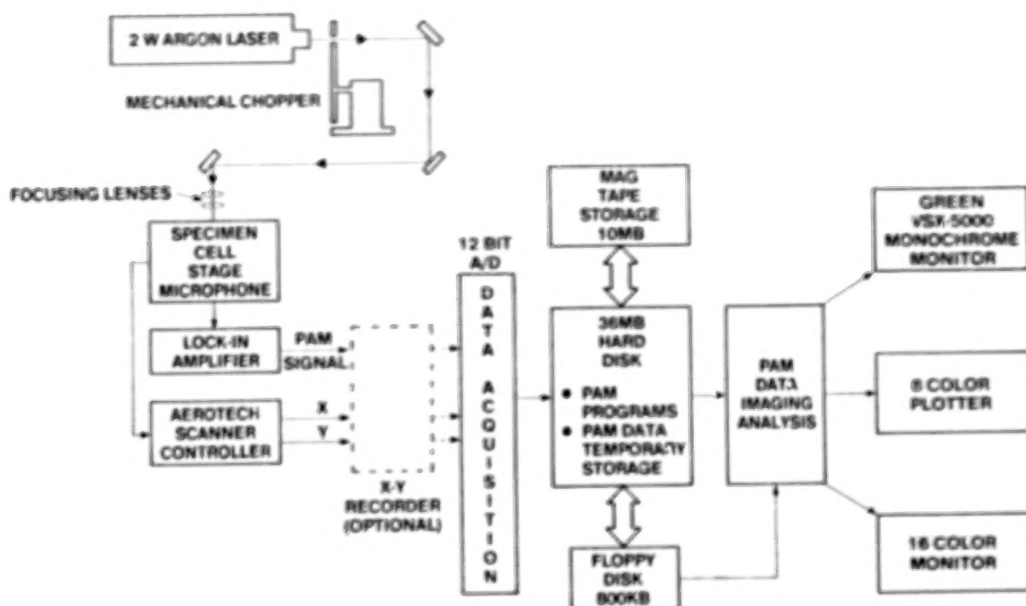
OBJECTIVES

- o DEVELOP COMPUTERIZED CAPABILITY TO DIGITALLY ACQUIRE/RETRIEVE AND IMAGE PAM SIGNALS
- o DEVELOP CAPABILITY TO DETECT 250 μ m SIZE VOIDS/INCLUSIONS 1mm BELOW INTERROGATING SURFACE
- o DEVELOP CAPABILITY TO DETECT SURFACE CONNECTED CRACKS
- o DEMONSTRATE ABILITY OF NDE TO PREDICT FAILURE SITE ON MOR BAR CONTAINING NATURAL FLAWS

NDE OF STRUCTURAL CERAMICS BY PHOTOACOUSTIC MICROSCOPY



PAM FLAW DETECTION DATA ACQUISITION AND IMAGING SYSTEM



PAM DATA ACQUISITION AND IMAGING-ANALYSIS SYSTEM

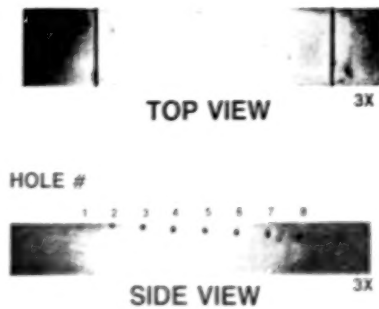
DATE
4/10/86
CHART NO.
PKK

FEATURES

- o SCANNER
 - o PROGRAMMABLE X-Y RASTER SCAN
 - o 2µm AXIS RESOLUTION
- o DATA ACQUISITION/IMAGING
 - o MENU DRIVEN ALGORITHMS
 - o ACQUIRES AND STORES DATA
 - o 12 BIT A/D RESOLUTION
 - o MONOCROME AND COLOR DISPLAY
 - o 8 COLOR PLOTTER
 - o EXPERIMENTAL STATISTICS
 - o MAGNIFICATION/ZOOM
 - o PAN
 - o THRESHOLDING
 - o FLAW/PAM SIGNAL SIZING
 - o HISTOROGRAM OF PAM SIGNALS

(148-42)0408-20

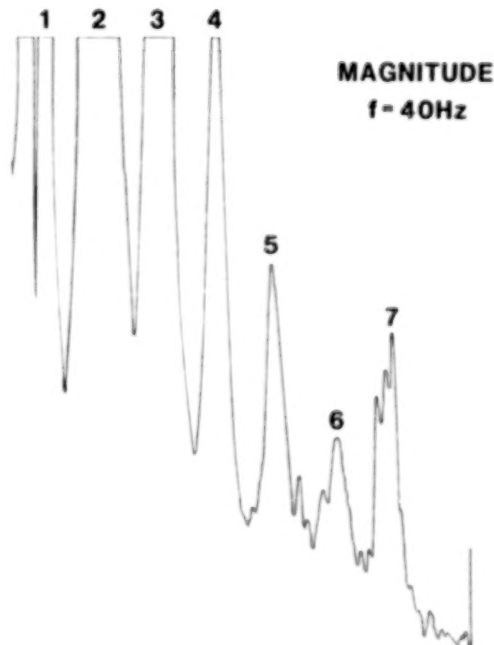
PAM FLAW DETECTION BATCH-A AS-FIRED Si₃N₄



HOLE #	HOLE LOCATION FROM TOP SURFACE μm
1	OPEN TO SURFACE
2	VERY NEAR TO SURFACE BUT NOT OPEN
3	156
4	390
5	547
6	665
7	825
8	1015

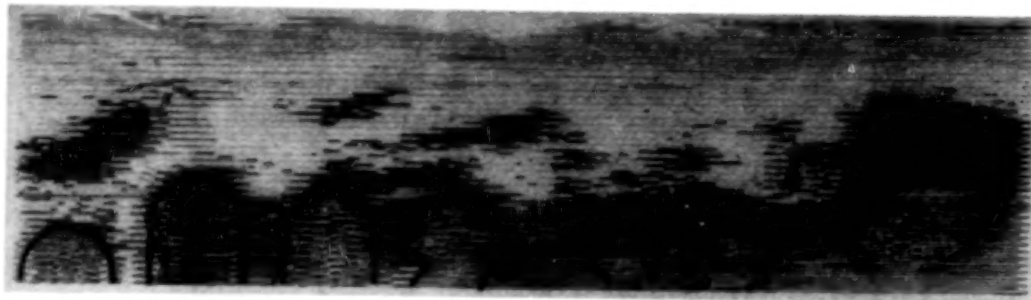
NOMINAL DIAMETER $\approx 375\mu\text{m}$
 NOMINAL DISTANCE BETWEEN HOLES $\approx 2.5\text{ mm}$
 APPROXIMATE DEPTH $\approx 3.125\text{ mm}$

PAM SUBSURFACE FLAW DETECTION AS-FIRED SILICON NITRIDE



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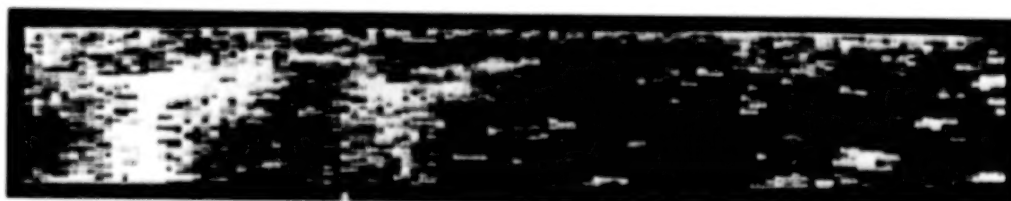
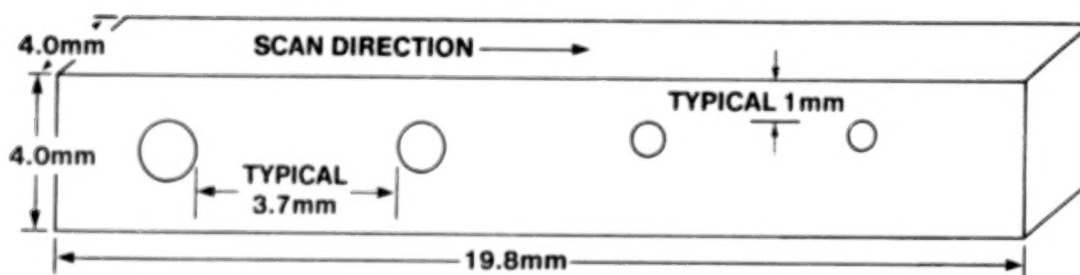
**PAM DIGITAL IMAGING-
SUBSURFACE FLAWS
BATCH-A AS-FIRED Si_3N_4**



1 2 3 4 6 7
HOLE #

2 mm

**PAM SUBSURFACE FLAW DETECTION
AS FIRED SINTERED SILICON CARBIDE**



HOLE
DIA. μm

1000

750

500

250

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION

DATE
4/10/86
CHART NO.
PKK

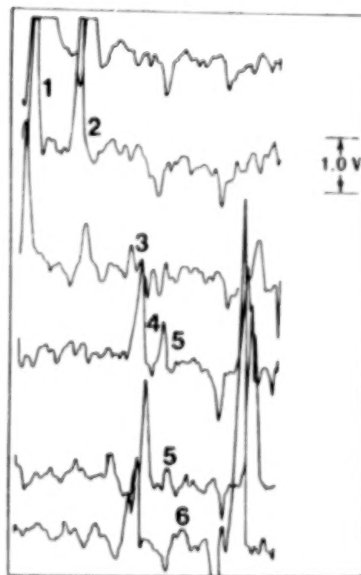
Crack #	Load (Kg)	Crack		Signal-to-Noise Ratio	
		Length (2c) μm	Depth ^a (a) μm	40 Hz 250 μm/sec. 200 μV	300 Hz 250 μm/sec. 50 μV
1	12	401	200	Saturated	Saturated
2	10	323	162	9.0	13.5
3	5	234	117	2.0	4.5
4	4	205	102	3.0	5.5
5	2	140	70	N.D.	2.0
6	1	96	48	N.D.	N.D.

*Assuming semicircular flaw, $a = c$

N.D. - Signal-to-noise ratio of 1
Difficult to separate the flaw signal from the background

CT-806(7-86)

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION



40 Hz

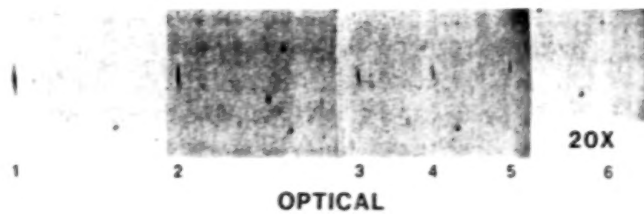


300 Hz

VS86-1810

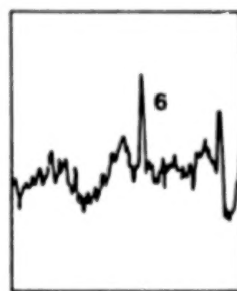
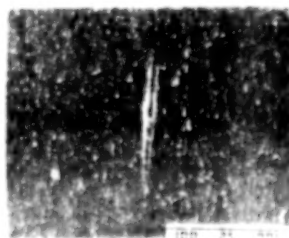
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PHOTOACOUSTIC MICROSCOPY SURFACE CRACK DETECTION



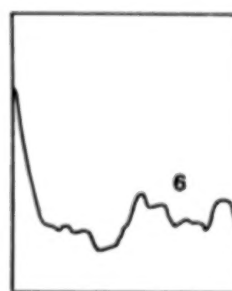
V586-1811

PHOTOACOUSTIC MICROSCOPY SURFACE CRACK DETECTION



50 μ m/SEC

HPSi₃N₄
f=40Hz



250 μ m/SEC

V586-1812

N88-23885

D13-27
P. 16

MOLTEN SALT CORROSION OF SIC AND Si_3N_4

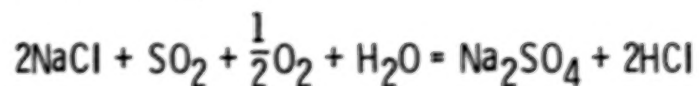
N. S. Jacobson, J. L. Smialek, and D. S. Fox
NASA Lewis Research Center
Cleveland, Ohio

The most severe type of corrosion encountered in heat engines is corrosion by molten sodium sulfate, which is formed by the reaction of ingested sodium chloride and sulfur impurities in the fuel. This problem has been studied extensively for superalloys, but only recently examined for ceramics. Our program at Lewis addresses this problem with laboratory studies to understand the fundamental reaction mechanisms and with burner studies to provide a more realistic simulation of the conditions encountered in a heat engine. In addition we are assessing the effect of corrosion on the strengths of these materials. Each of these aspects will be reviewed and some ideas toward possible solutions will be discussed.

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THE HOT CORROSION PROBLEM

- FORMATION OF Na_2SO_4



- DEPOSITION OF MOLTEN Na_2SO_4 ON ENGINE PARTS
FUNCTION OF T, P, [SALT]

- POTENTIALLY CATASTROPHIC ATTACK

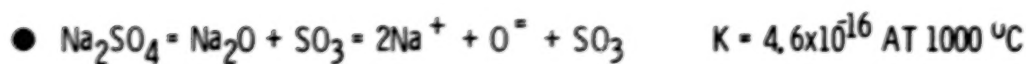
CS-86-1388

TURBINE VANE HOT CORROSION



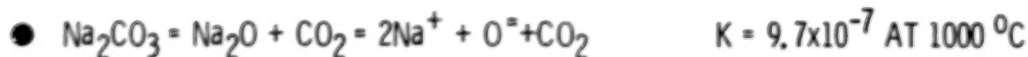
CS-73740

BASIC AND ACIDIC MOLTEN SALTS



LOW P_{SO_3} - HIGH $a_{\text{O}^{2-}}$ - BASIC

HIGH P_{SO_3} - LOW $a_{\text{O}^{2-}}$ - ACIDIC



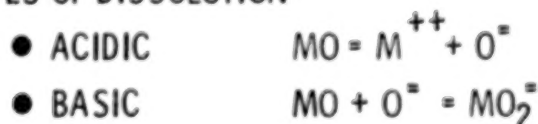
MODEL BASIC SALT

CS-86-1383

REACTIONS WITH MOLTEN SALTS

- DISSOLUTION OF PROTECTIVE OXIDE (MO) BY MOLTEN SALT
- UNPROTECTED METAL OR CERAMIC SUSCEPTIBLE TO ATTACK

● TYPES OF DISSOLUTION



● SiO_2 IS AN ACIDIC OXIDE

- EXPECT REACTION WITH BASIC SALT
- $\text{SiO}_2 + \text{O}^{2-} = \text{SiO}_3^{2-}$
- SILICATES LIQUID T 780°C

CS-86-1384

EXPERIMENTAL TECHNIQUES

● LABORATORY

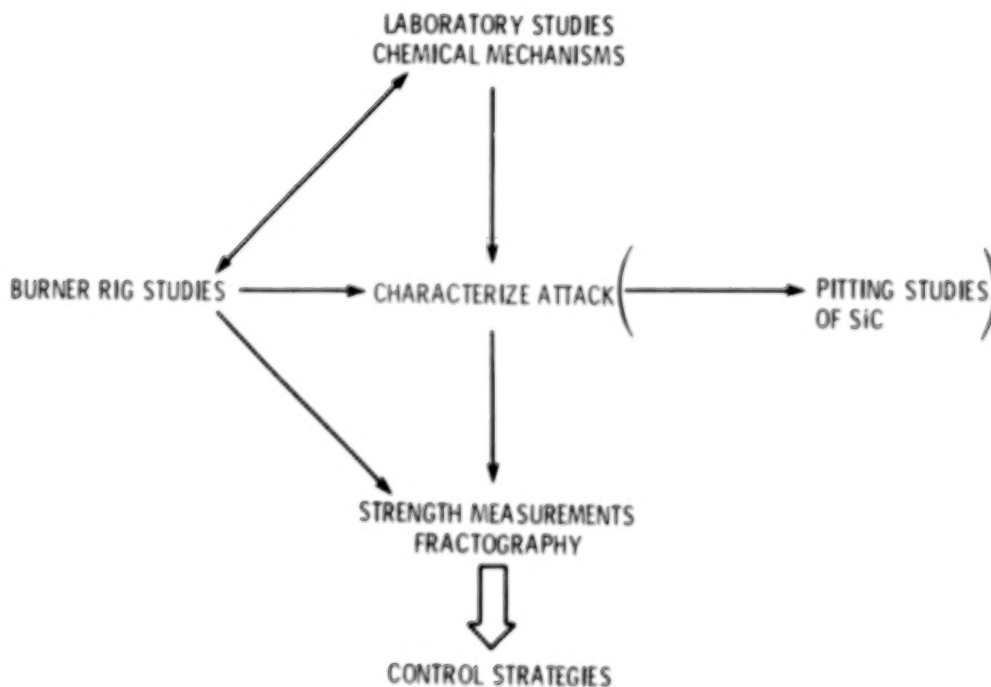
- AIRBRUSH SAMPLE WITH SALT; HEAT
- PRECISELY CONTROL PARAMETERS
- MONITOR KINETICS, MICROSTRUCTURAL CHANGES
- ONE TIME DEPOSITION OF SALT

● BURNER

- JET FUEL SEEDED WITH NaCl
- CONTINUOUS DEPOSITION OF SALT; CLOSER TO ENGINE CONDITIONS
- DIFFICULT TO CONTROL PARAMETERS

CS-86-1382

LEWIS CORROSION STUDIES OF SiC AND Si₃N₄



CS-86-1379

MATERIALS STUDIED

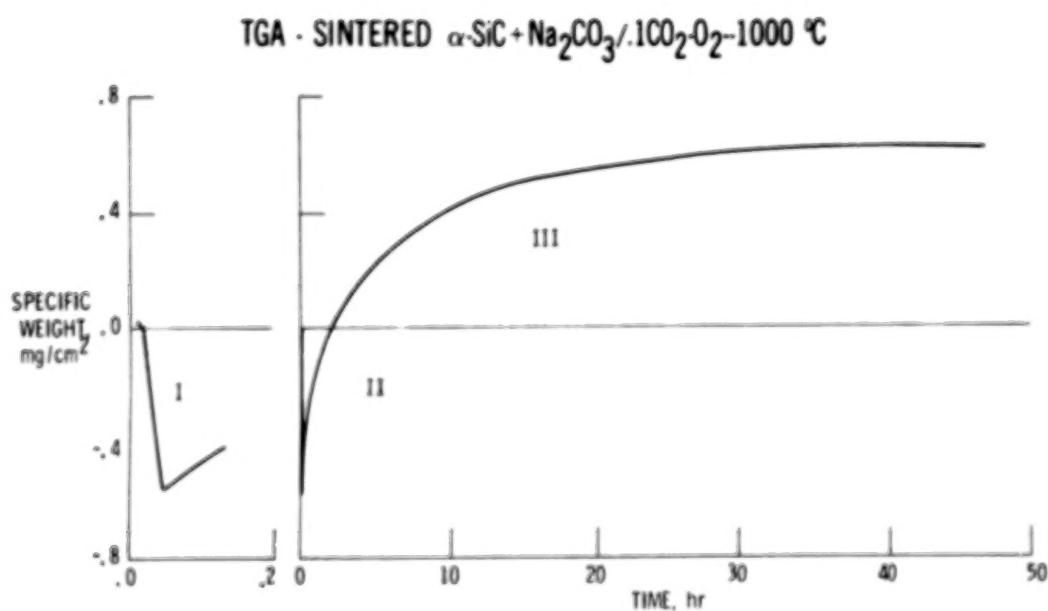
- SINTERED α -SiC (B, C)

HP SiC, CVD SiC, SC SiC

- SINTERED Si_3N_4 (Al_2O_3 , Y_2O_3)

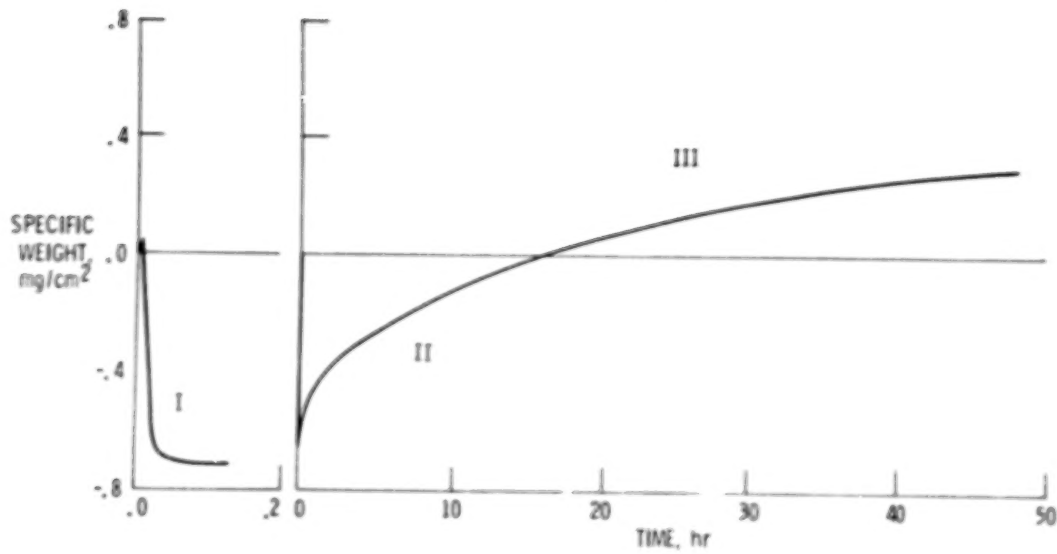
SINTERED Si_3N_4 (Y_2O_3), HIP'd RB Si_3N_4

CS-86-1386

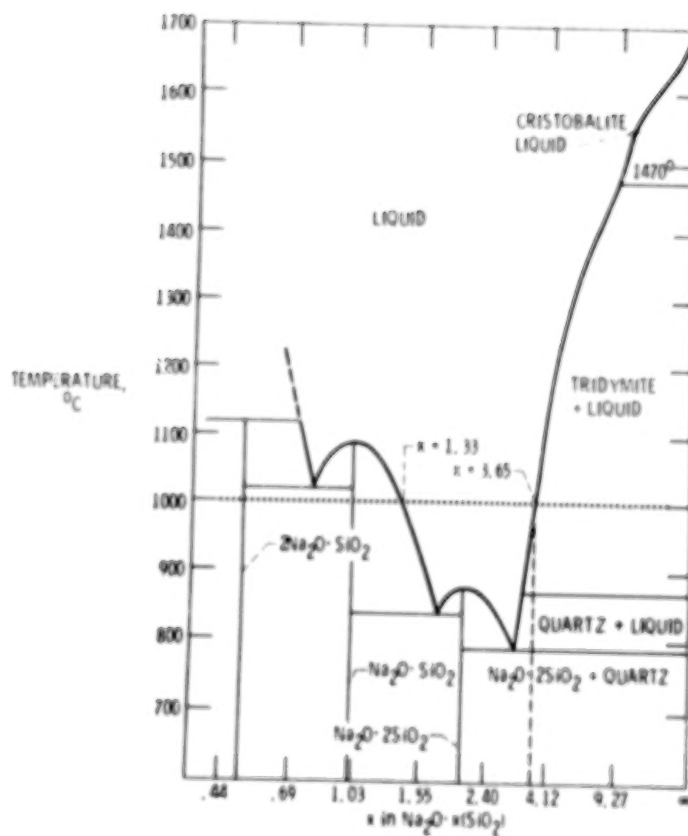


CS-86-1377

TGA - HIP'D RBSN + $\text{Na}_2\text{CO}_3/\text{O}_2$ -1000 °C



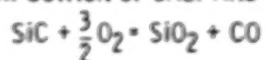
CS-84-1378



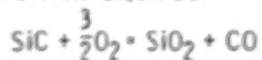
CS-85-0793

MECHANISM OF CORROSION BY Na_2CO_3

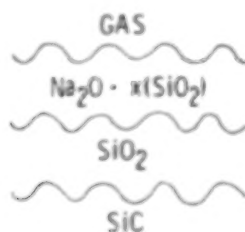
I. DECOMPOSITION OF SALT AND SILICATE FORMATION



II. MOVE TOWARD LIQUIDUS



III. GROWTH OF PROTECTIVE SiO_2 LAYER-SLOWING OF REACTION



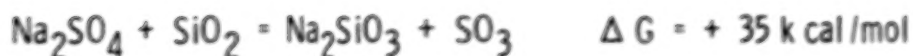
CS-86-1380

Na_2CO_3 VERSUS $\text{Na}_2\text{SO}_4/\text{O}_2$

- $\text{Na}_2\text{SO}_4 = \text{Na}_2\text{O} + \text{SO}_3^\dagger$ BASIC MOLTEN SALT
- SiC - SIMILAR BEHAVIOR
- Si_3N_4 - $\text{Na}_2\text{SO}_4/\text{O}_2$ CORROSION IS SLOWER THAN $\text{Na}_2\text{CO}_3/\text{O}_2$
- IMPORTANT SYSTEM - CLOSE TO BURNER RIG

CS-86-1381

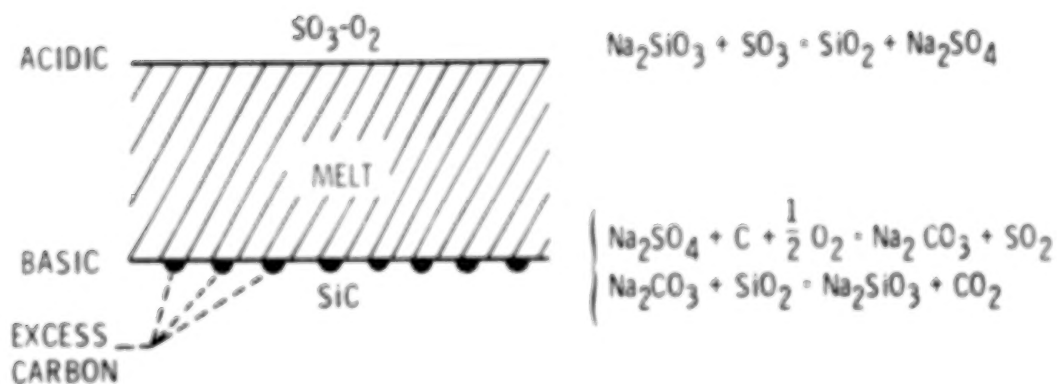
Na₂SO₄ / SO₃ CASE



- $P_{\text{SO}_3} > 10^{-6} \text{ atm}$ -- NO REACTION
- $\text{Na}_2\text{SO}_4 / 10^{-4} \text{ SO}_3\text{-O}_2$ DOES NOT ATTACK
 - QUARTZ
 - HOT PRESSED (Al₂O₃) SiC
 - SINGLE CRYSTAL SiC
 - PREOXIDIZED (1400 °C - 23 h) SINTERED SiC
- $\text{Na}_2\text{SO}_4 / 10^{-4} \text{ SO}_3\text{-O}_2$ DRAMATICALLY ATTACKS AS-GROUND SINTERED SiC

CS-85-2269

BASIC/ACIDIC CHARACTER OF MELT



ESTABLISHES FLUXING CONDITION

CS-85-2266

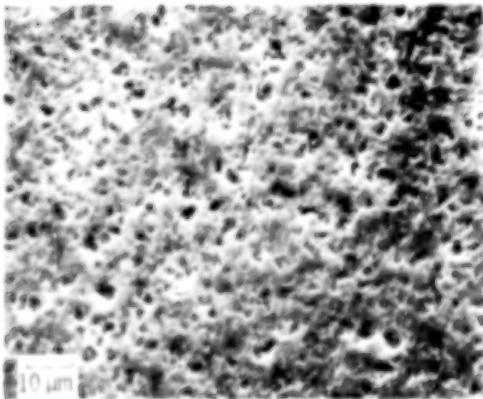
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ATTACK OF CERAMIC SUBSTRATE

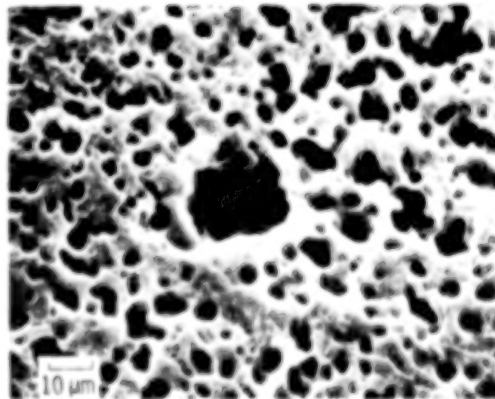
- HF REMOVES GLASSY PRODUCT LAYERS
(CAUTION WITH Si_3N_4)
- ATTACK DOES NOT OCCUR BY EVEN RECESSION
- SiC - SEVERE PITTING ATTACK
 $\text{Na}_2\text{CO}_3 < \text{Na}_2\text{SO}_4/\text{O}_2 < \text{Na}_2\text{SO}_4/\text{SO}_3$
- Si_3N_4 - SEVERE GRAIN BOUNDARY ATTACK

CS-86-1385

CORROSION PITTING



SINTERED α -SiC BEFORE CORROSION

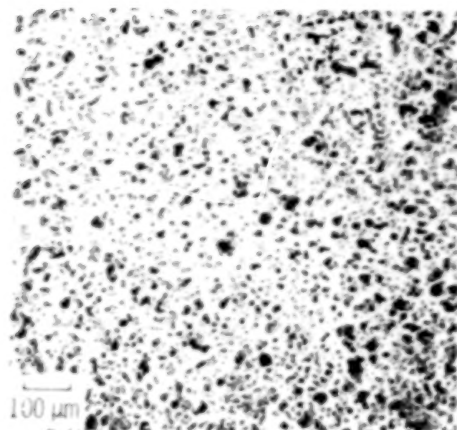


SiC AFTER CORROSION
 $\text{Na}_2\text{CO}_3/\text{CO}_2$ - 48 hrs - 1000 °C
PRODUCTS REMOVED WITH HF

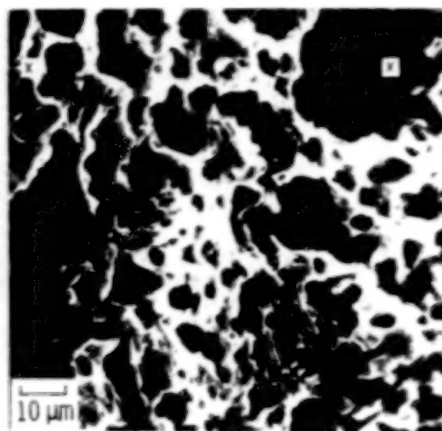
CS-85-3407

PITTING ATTACK MORPHOLOGY AFTER $\text{Na}_2\text{SO}_4/\text{SO}_3$ CORROSION

SCALE REMOVED BY HF DISSOLUTION



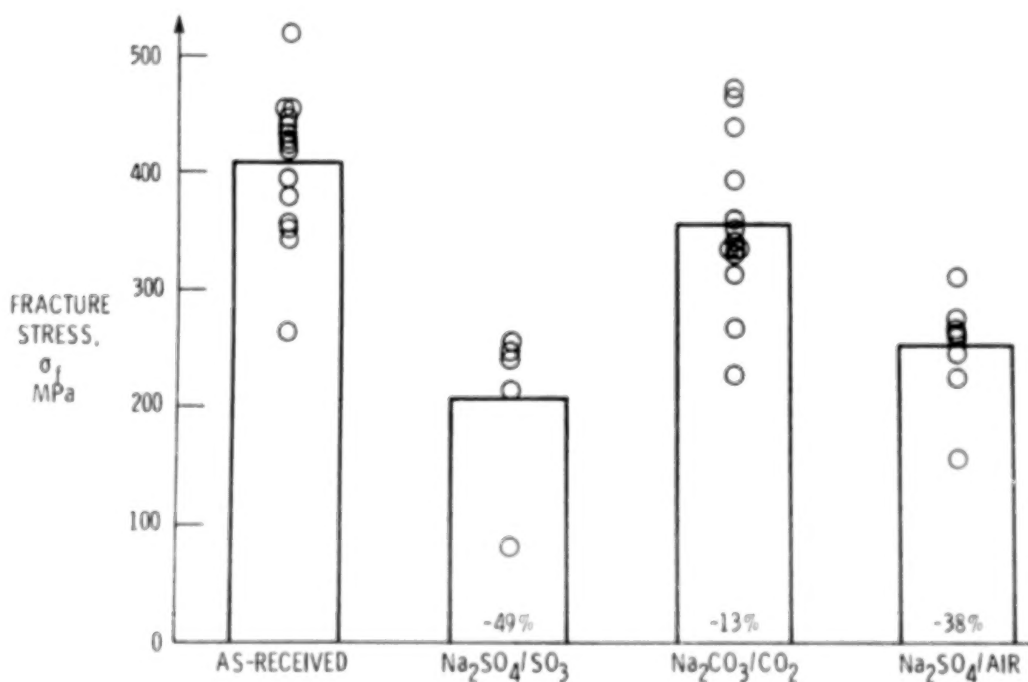
UNIFORM PITTING OBSERVED
OVER LARGE AREAS



DETAIL OF (a) SHOWING HONEYCOMB
PIT STRUCTURE

CS-85-2307

STRENGTH DEGRADATION OF α -SiC AFTER FURNACE CORROSION TESTING



CS-85-2336

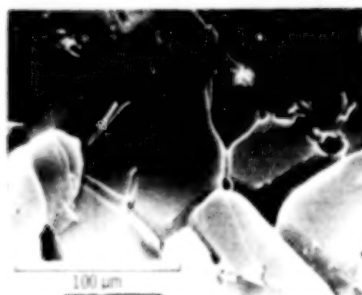
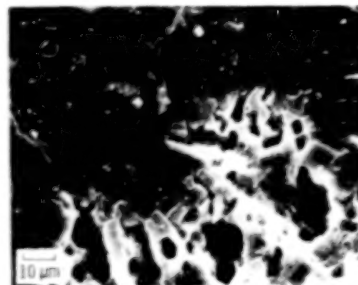
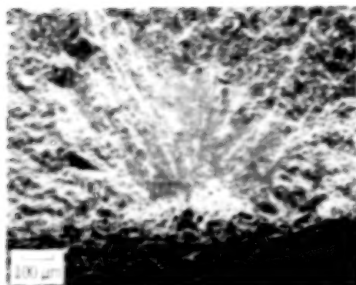
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FRACTURE ORIGIN, PITTING, AND GRAIN BOUNDARY ATTACK AFTER
 $\text{Na}_2\text{SO}_4/\text{SO}_3$ CORROSION

SCALE REMOVED BY HF

$\sigma_f = 188 \text{ MPa}$

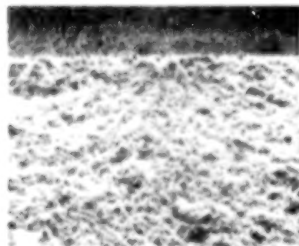
PIT DEPTH = $113 \mu\text{m}$



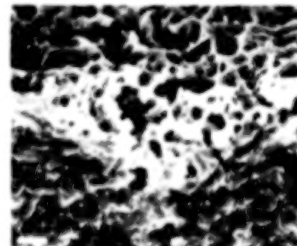
CS-84-4452

CORROSION PIT FRACTURE ORIGIN AFTER Na_2SO_4 /AIR CORROSION

SCALE REMOVED BY HF DISSOLUTION; $\sigma_f = 373 \text{ MPa}$, PIT DEPTH = $40 \mu\text{m}$



RADIAL CRACK LINES POINTING
TO CORROSION PIT

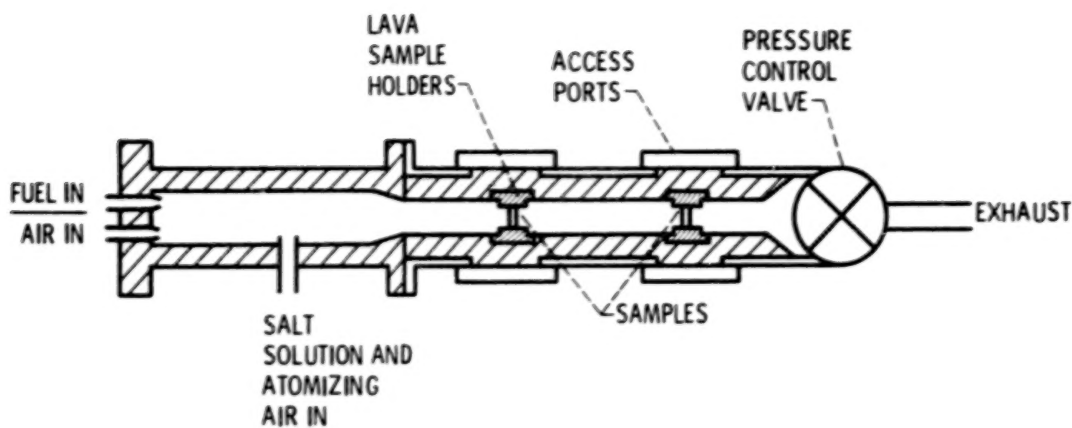


INTERSECTION OF DEEPLY PITTED
REGION WITH FRACTURE SURFACE



GRANULAR ATTACK MORPHOLOGY
IN PIT

CS-85-2305



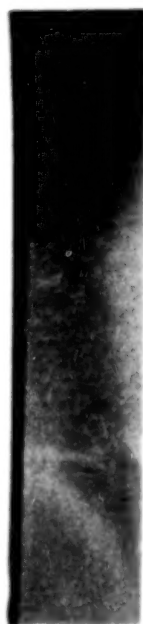
- PARALLEL TO $\text{Na}_2\text{SO}_4/\text{O}_2$ FURNACE STUDY
- CONTINUOUS SOURCE OF Na_2O
- CONTINUOUS $\text{Na}_2\text{O} \cdot x(\text{SiO}_2)$ FORMATION

OPERATING PARAMETERS

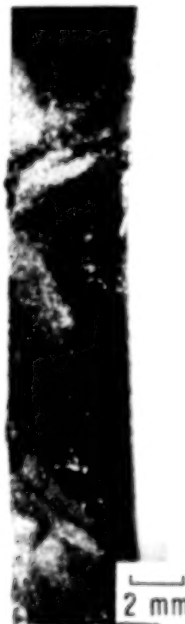
- $T = 990 \pm 10^\circ\text{C}$
- JET A FUEL - 0.05% S
- 4 ppm Na AS NaCl
- FLOW VELOCITY - 310 ft/sec

CS-86-1376

BURNER RIG TESTS OF $\alpha\text{-SiC}$ AT 1000°C



NO SALT
46 hr



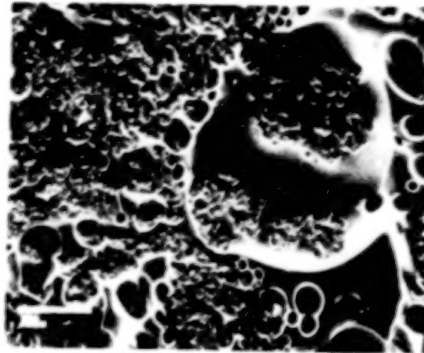
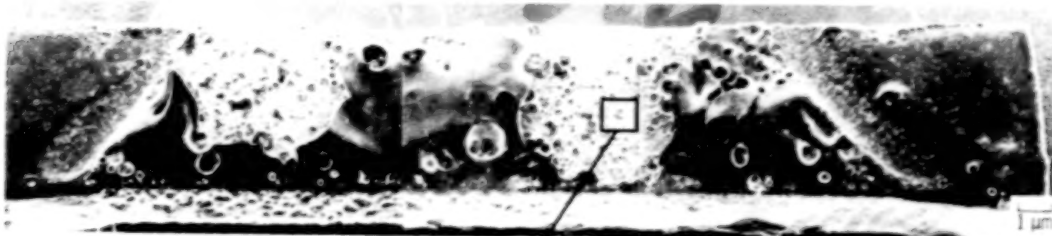
4 ppm Na
13.5 hr

AIR FLOW →

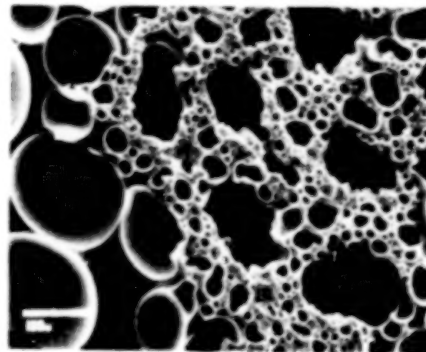
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EXTENSIVE BUBBLE FORMATION IN BURNER RIG SAMPLES
MECHANICAL SCALE REMOVAL



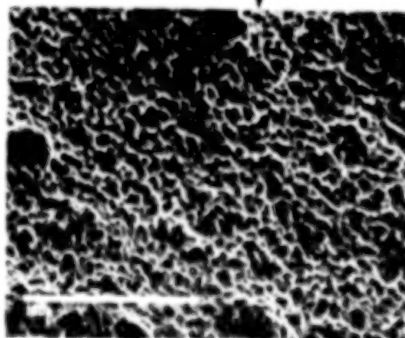
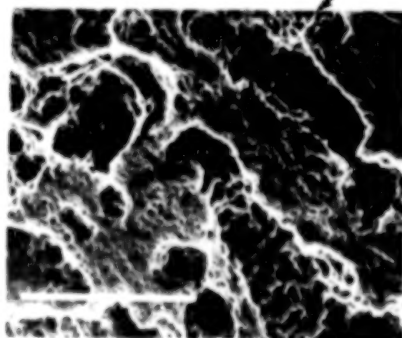
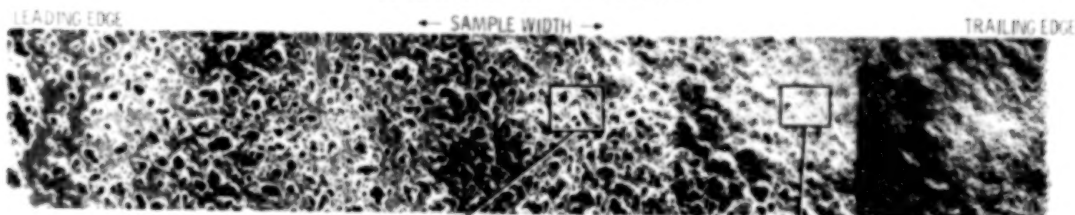
INTACT SCALE REMAINING



UNDERSIDE OF SPALLED SCALE

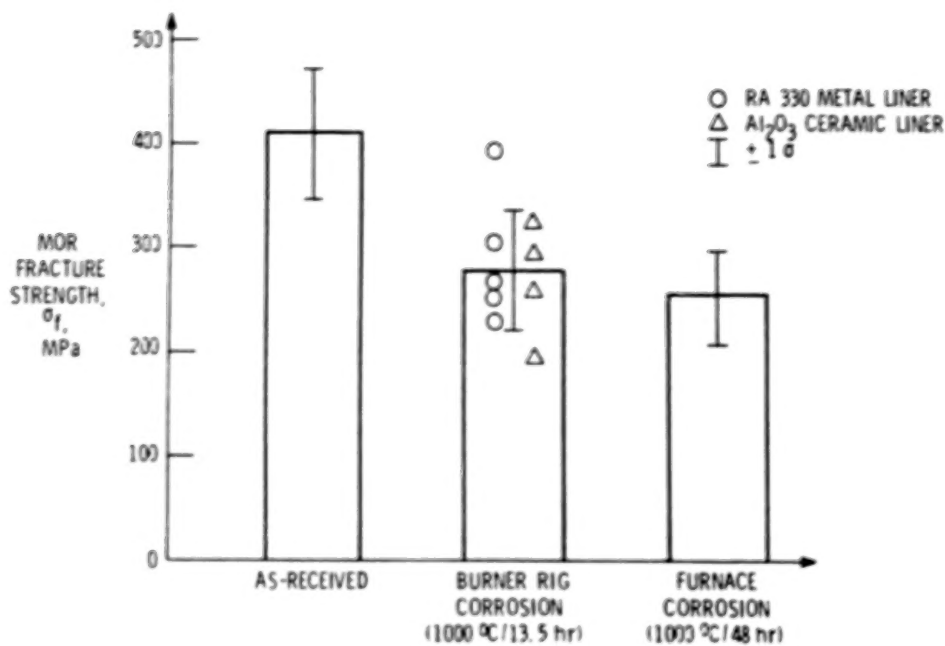
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α -SiC PITTING MORPHOLOGY CAUSED BY BURNER RIG CORROSION
SCALE REMOVED BY HF DISSOLUTION



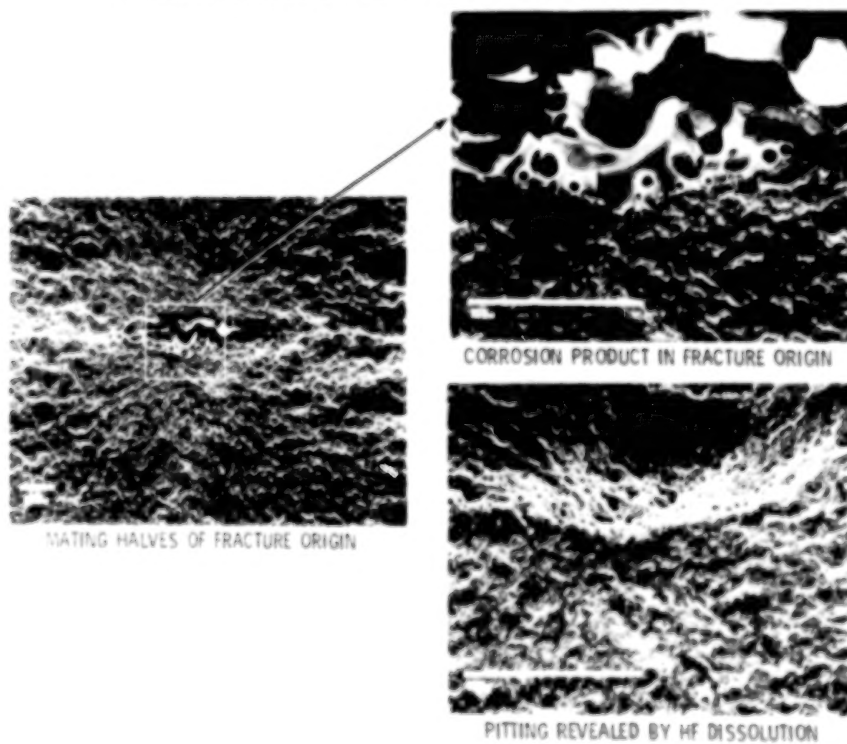
CS-85-1207

EFFECT OF BURNER RIG HOT CORROSION ON ROOM TEMPERATURE α -SiC STRENGTH



CS-85-1324

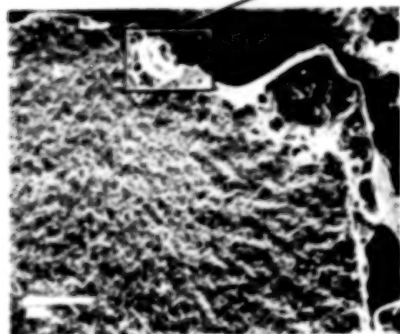
FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN



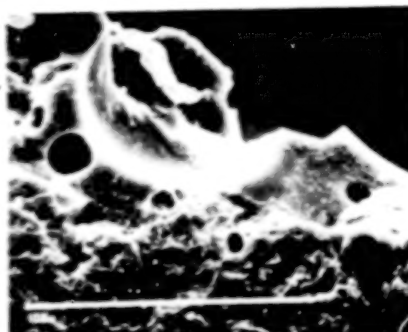
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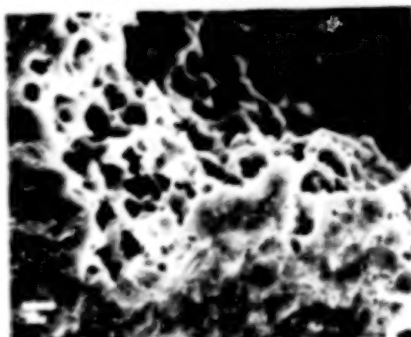
FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN



CRACK LINES RADIATE FROM CORNER
CORROSION PIT



BUBBLE FORMATION AT INTERFACE



PITTING REVEALED BY HF DISSOLUTION

CS-85-1204

SUMMARY

LABORATORY STUDIES

- BASIC MOLTEN SALTS
 SiO_2 FORMATION AND DISSOLUTION TO LIQUIDUS
- ACIDIC MOLTEN SALTS
 NO ATTACK, UNLESS BASIC CONDITIONS AT MELT BOTTOM

BURNER RIG

- PARALLEL TO $\text{Na}_2\text{SO}_4/\text{O}_2$ - BASIC SALT ATTACK
- CONTINUOUS $\text{Na}_2\text{O} \cdot x(\text{SiO}_2)$ FORMATION

ATTACK OF CERAMICS

- SiC -- SEVERE PITTING -- UP TO 50% STRENGTH REDUCTION
- Si_3N_4 - SEVERE GRAIN BOUNDARY ATTACK -- WORK IN PROGRESS

SUMMARY AND CONTROL STRATEGIES

- MOLTEN SALT CORROSION
 - CAN BE CATASTROPHIC
 - ENGINEERS MUST BE AWARE CERAMICS, LIKE SUPERALLOYS, ARE SUSCEPTIBLE
- CONTROL STRATEGIES
 - WORK OUTSIDE SALT DEPOSITION REGIME
 - MAKE SALTS ACIDIC
 - COATINGS; MODIFY SiO_2 LAYER

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P-9

**THERMAL CYCLIC DURABILITY TESTING OF CERAMIC
MATERIALS FOR TURBINE ENGINES**

L.J. Lindberg

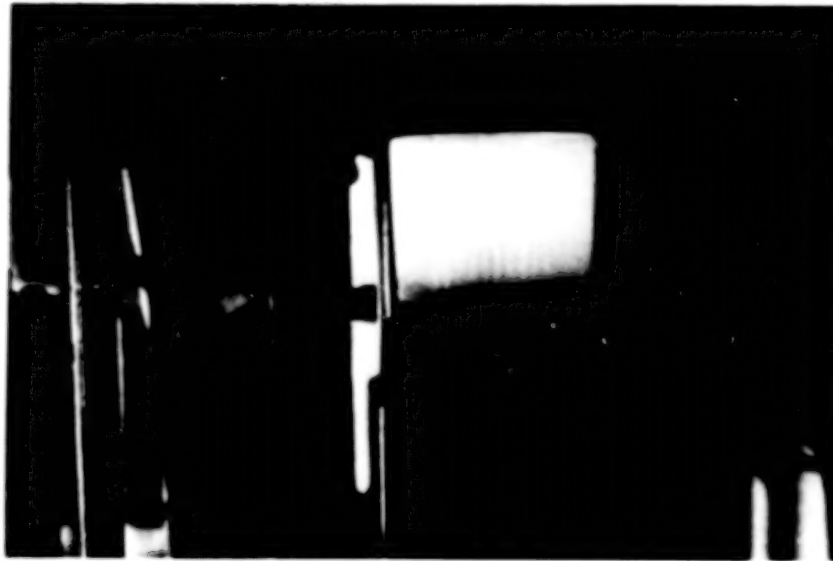
**Garrett Turbine Engine Company
Phoenix, Arizona 85010**

The thermal cyclic durability of commercial ceramic materials for turbine engines has been under evaluation since 1978. Ceramic materials are exposed to cyclic diesel-fired burner exhaust at either 1204 or 1371C (2200 or 2500F) for up to 3500 hours. The test conditions are selected to simulate the environment experienced by the hot flow path components in an automotive gas turbine engine. The silicon nitride and silicon carbide materials tested are the same ceramic materials currently used on the AGT100 and AGT101 ceramic turbine engine programs.

This work was performed under the NASA funded program, 3500-Hour Durability Testing of Commercial Ceramic Materials, Contract DEN3-27.

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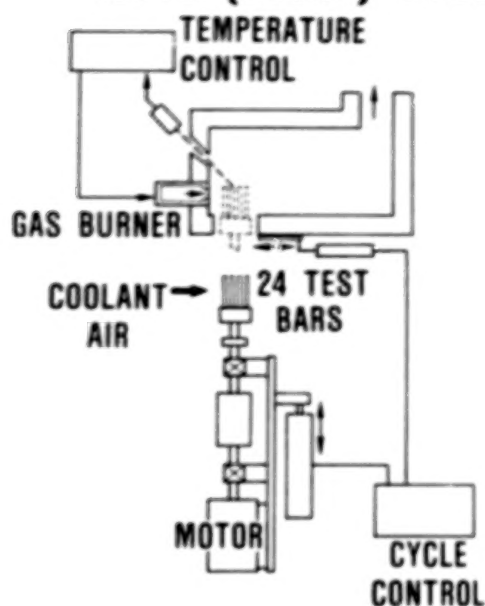
THERMAL CYCLIC DURABILITY TESTING OF CERAMIC MATERIALS FOR TURBINE ENGINES



3500-HOUR DURABILITY TESTING OF COMMERCIAL CERAMIC MATERIALS

- OBJECTIVE
 - DETERMINE LONG-TERM DURABILITY OF CERAMIC GAS TURBINE ENGINE MATERIALS
- APPROACH
 - CYCLE CERAMIC TEST BARS FROM HIGH TEMPERATURE BURNER EXHAUST TO COLD AIR
 - MONITOR CHANGES IN STRENGTH, WEIGHT, AND DIMENSIONS WITH EXPOSURE TIME AND COMPARE TO BASELINE PROPERTIES
 - TESTING IS TERMINATED WHEN THE STRENGTH IS REDUCED TO 50 PERCENT OF THE BASELINE STRENGTH
- BENEFITS
 - IDENTIFIES CERAMIC MATERIALS CAPABLE OF LONG-TERM USE IN GAS TURBINE ENGINE
 - PROVIDES DIRECT COMPARISON OF NEW CERAMICS WITH MATERIALS PREVIOUSLY TESTED IN THIS CONTINUING PROGRAM

NASA/GARRETT FACILITY DEVELOPED FOR 1371C (2500F) CYCLIC DURABILITY TESTING



CERAMIC TEST BAR
DURABILITY TEST FACILITY

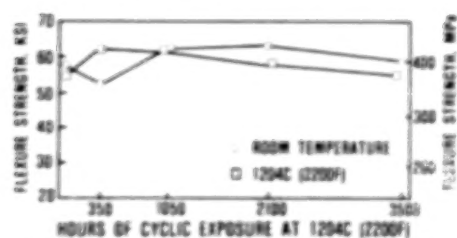


AIR COOLED CERAMIC TEST
BAR HOLDER

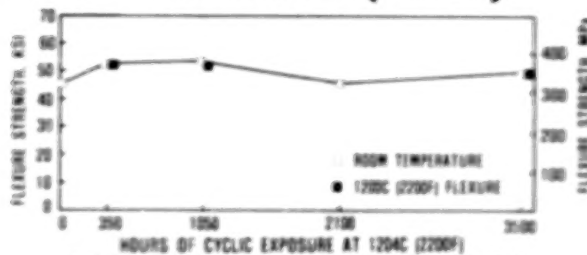
A VARIETY OF CERAMICS HAVE BEEN DURABILITY TESTED

MATERIAL	TEMP. C (F)	DURABILITY, HOURS
SOHIO SINTERED ALPHA SILICON CARBIDE (SASC)	1204 (2200)	3500
SOHIO REACTION SINTERED SILICON CARBIDE (RSSC)	1204 (2200)	3500
ACC RBN 101 REACTION BONDED SILICON NITRIDE (RBSN)	1204 (2200)	2100
REFEL SILICONIZED SILICON CARBIDE (SiSC)	1204 (2200)	2100
NGK SN-50 SINTERED SILICON NITRIDE (SSN)	1204 (2200)	<350
GTE AY6 SSN	1204 (2200)	<350
TOSHIBA SSN	1204 (2200)	<350
ACC SSN	1204 (2200)	<350
NORTON NCX 34 HOT PRESSED SILICON NITRIDE (HPSN)	1204 (2200)	<100
SOHIO SASC	1371 (2500)	3500
ACC RBSN	1371 (2500)	2100
REFEL SiSC	1371 (2500)	<350

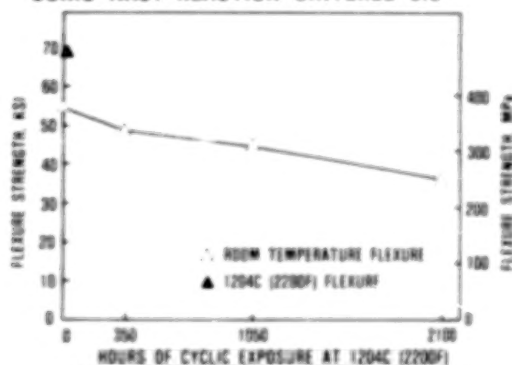
SEVERAL CERAMIC MATERIALS DEMONSTRATE ACCEPTABLE PERFORMANCE AT 1204C (2200F)



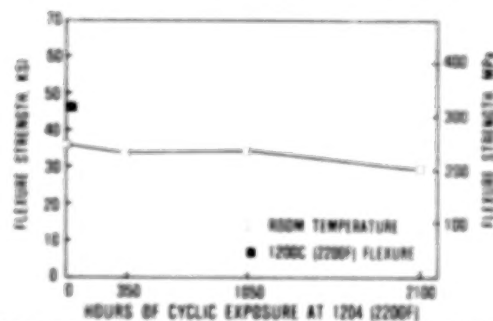
SOHIO KX01 REACTION SINTERED SiC



SOHIO SINTERED ALPHA SILICON CARBIDE



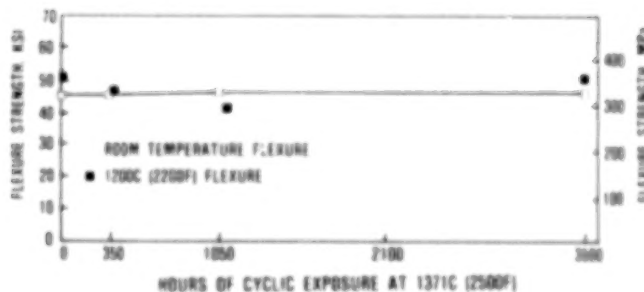
REFEL SILICONIZED SILICON CARBIDE



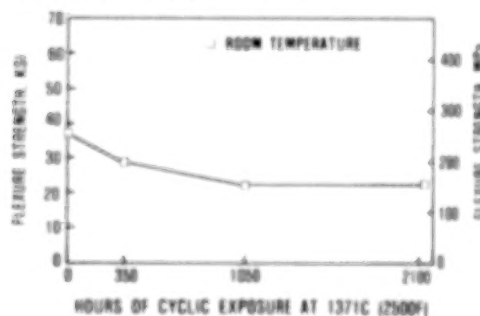
ACC RBN101 REACTION BONDED SILICON NITRIDE

TEST RESULTS SHOW CERAMIC DURABILITY AT 1371C (2500F)

SOHIO SINTERED
ALPHA SILICON CARBIDE



ACC RBN101 REACTION BONDED SILICON NITRIDE



NEW MATERIALS ARE TESTED AS THEY BECOME AVAILABLE

- KYOCERA SC201 SINTERED SILICON CARBIDE (SSC) — DURABILITY TESTING IN PROGRESS
- SOHIO SASC (INJECTION MOLDED, AS-FIRED SURFACES) — DURABILITY TESTING IN PROGRESS
- GE β SSC — BASELINE TESTING COMPLETE
- CORNING LAS — BASELINE TESTING COMPLETE
- NGK SN-82 SSN — BASELINE TESTING COMPLETE
- ACC CODE 2 SSN — TO BE PROCURED
- KYOCERA SN 250M OR 270M SSN — TO BE PROCURED

BASELINE STRENGTH OF KYOCERA SINTERED SILICON CARBIDE HAS BEEN DETERMINED

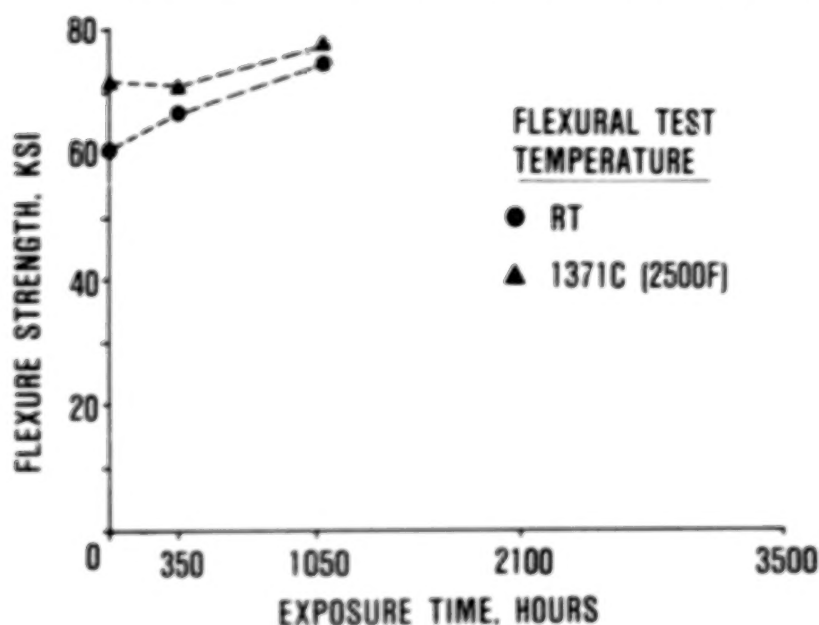
MATERIAL: KYOCERA SC201

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1204C (2200F)	1371C (2500F)
MEAN STRENGTH, KSI (12 DATA POINTS)	61.9	66.2	71.3
STANDARD DEVIATION, KSI	11.4	8.2	8.8

CYCLIC EXPOSURE TESTING IS BEING CONDUCTED AT 1371C (2500F)

KYOCERA SC201 HAS UNDERGONE 1050 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)



BASELINE STRENGTH OF SOHIO INJECTION MOLDED SINTERED SiC HAS BEEN DETERMINED

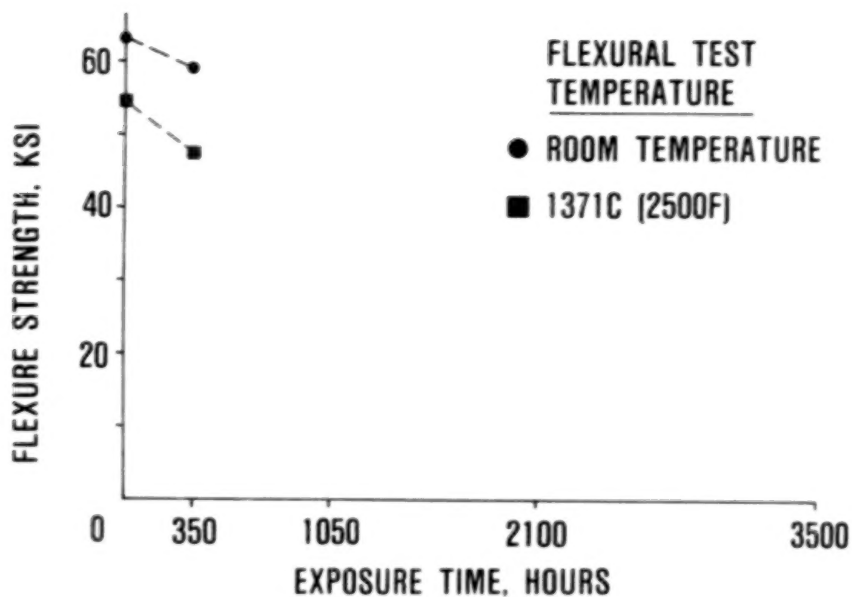
MATERIAL: SOHIO SASC

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1204C (2200F)
MEAN STRENGTH, KSI (12 DATA POINTS)	63.5	60.7
STANDARD DEVIATION, KSI	9.2	7.6

CYCLIC EXPOSURE TESTING IS BEING CONDUCTED AT 1371C (2500F)

SOHIO INJECTION MOLDED SASC HAS UNDERGONE 350 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)



BASELINE STRENGTH OF GE β SILICON CARBIDE HAS BEEN DETERMINED

MATERIAL: GE β SiC

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1371C (2500F)
MEAN STRENGTH, KSI (12 DATA POINTS)	61.4	61.2
STANDARD DEVIATION, KSI	4.6	8.9

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1371C (2500F)

BASELINE STRENGTH OF NGK SINTERED SILICON NITRIDE HAS BEEN DETERMINED

MATERIAL: NGK SN-82

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	982C (1800F)	1204C (2200F)
MEAN STRENGTH, KSI (12 DATA POINTS)	120.4	103.9	97.3
STANDARD DEVIATION, KSI	14.0	9.2	5.5

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1204C (2200F)

RESULTS

- SOHIO SASC (ISOPRESSED, MACHINED SURFACES) EXPERIENCES NO NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1371C (2500F)
- SOHIO RSSC EXPERIENCES NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)
- ACC RBSN EXPERIENCES A 20-PERCENT STRENGTH REDUCTION AT 1204C (2200F) AFTER 2100 HOURS OF EXPOSURE AND A 20-PERCENT STRENGTH REDUCTION AFTER 350 HOURS AT 1371C (2500F)
- ALL SSN MATERIALS TESTED TO DATE (NGK SN-50, ACC CODE 2, GTE AY6, TOSHIBA SSN) EITHER EXHIBITED LOW BASELINE FLEXURE STRENGTHS AND/OR SHOWED >50-PERCENT STRENGTH DEGRADATION DURING THE FIRST 350 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)

BASELINE FLEXURE STRENGTH AND CYCLIC DURABILITY TESTING IS SCHEDULED FOR 1986-1987

- CYCLIC EXPOSURE TESTING IS CURRENTLY BEING CONDUCTED ON INJECTION MOLDED SOHIO SASC WITH AS-FIRED SURFACES AND KYOCERA SSC WITH AS-FIRED SURFACES AT 1371C (2500F)
- CYCLIC EXPOSURE TESTING OF GE β SSC, CORNING LAS, NGK SN-82 SSN AND ACC CODE 2 SSN WILL BE CONDUCTED DURING 1986-1987
- KYOCERA SN-250M OR 270M WILL BE PROCURED FOR BASELINE AND EXPOSURE TESTING DURING 1986-1987

N88-23887

FRACTOGRAPHIC AND MICROSTRUCTURAL EVALUATION OF 3500-HOUR
DURABILITY SPECIMENS

A. D. Miller
Materials Science and Engineering
University of Washington
Seattle, Washington 98195

NASA Lewis Research Center has since 1978 contracted with Garrett Turbine Engine Company to conduct long-term durability testing of candidate ceramic materials for advanced gas turbine applications. Specimens of the materials are exposed to combustion atmospheres under temperature cyclic conditions for times up to 3500 hours and at peak temperatures of 1200 and 1370 C. The specimen strengths after exposure are measured at room temperature and at 1200 C. In addition, a number of physical measurements are taken, however no provision is made in the contract for microstructural examination of the specimens.

The work under this project covers examination of three materials, (1) sintered alpha silicon carbide manufactured by Carborundum Co., (2) sintered silicon nitride, manufactured by Toshiba, and (3) reaction bonded silicon nitride, grade RBN-104, manufactured by Airesearch Casting Company. The work required the development of sample preparation techniques to provide high quality thin-section specimens which can be examined by transmitted light or thinned using an ion mill for subsequent TEM examination.

Specimen preparation techniques and the results of optical and electron microscopic examination of the reaction interfaces of the selected specimens are presented and discussed.

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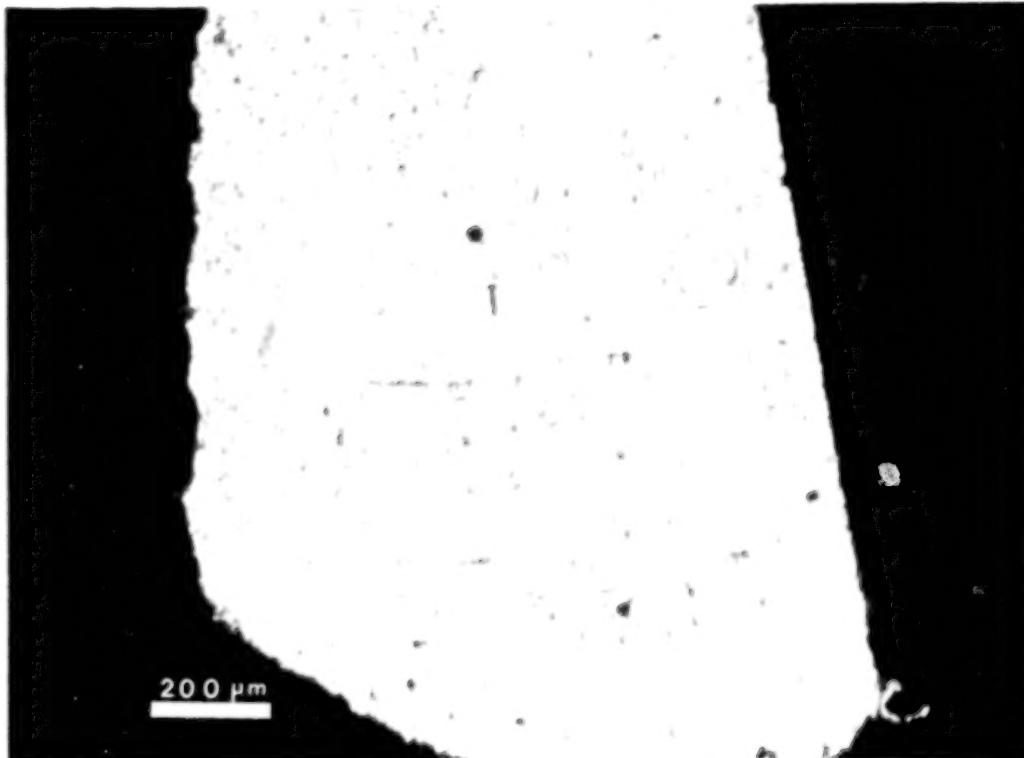


Figure 1. - Baseline SASC; crossed Nichols. 95X

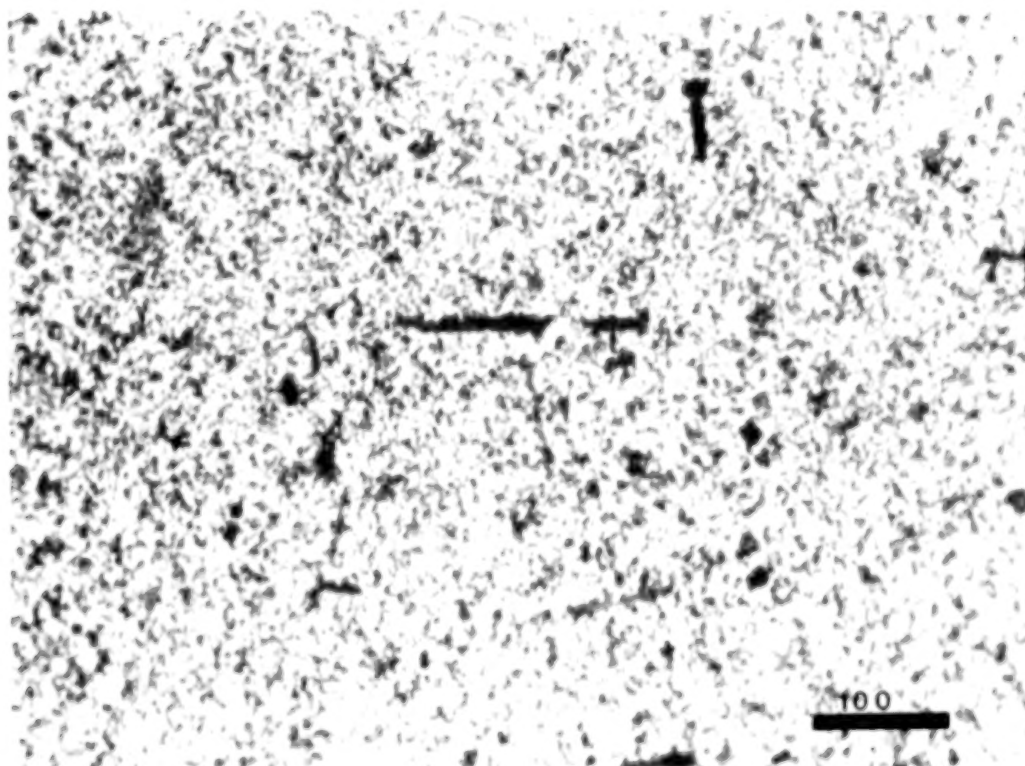


Figure 2. - Baseline SASC; crossed Nichols. 240X.

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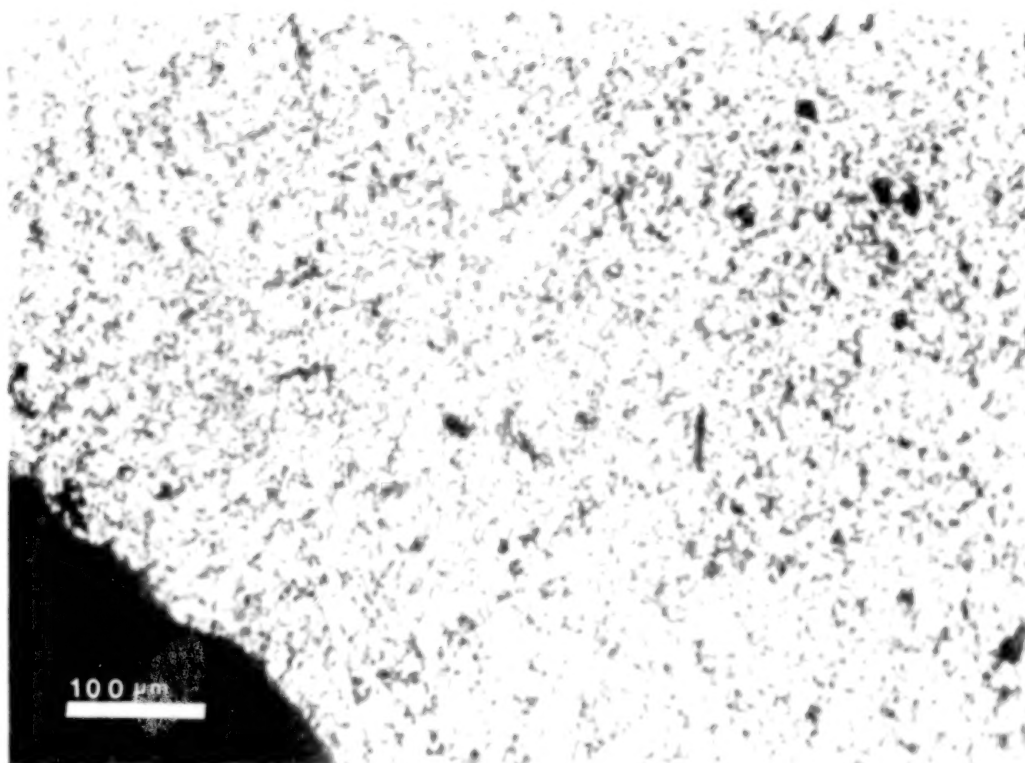


Figure 3. - Same field as fig.2; crossed Nichols, rotated 45°. 240X.

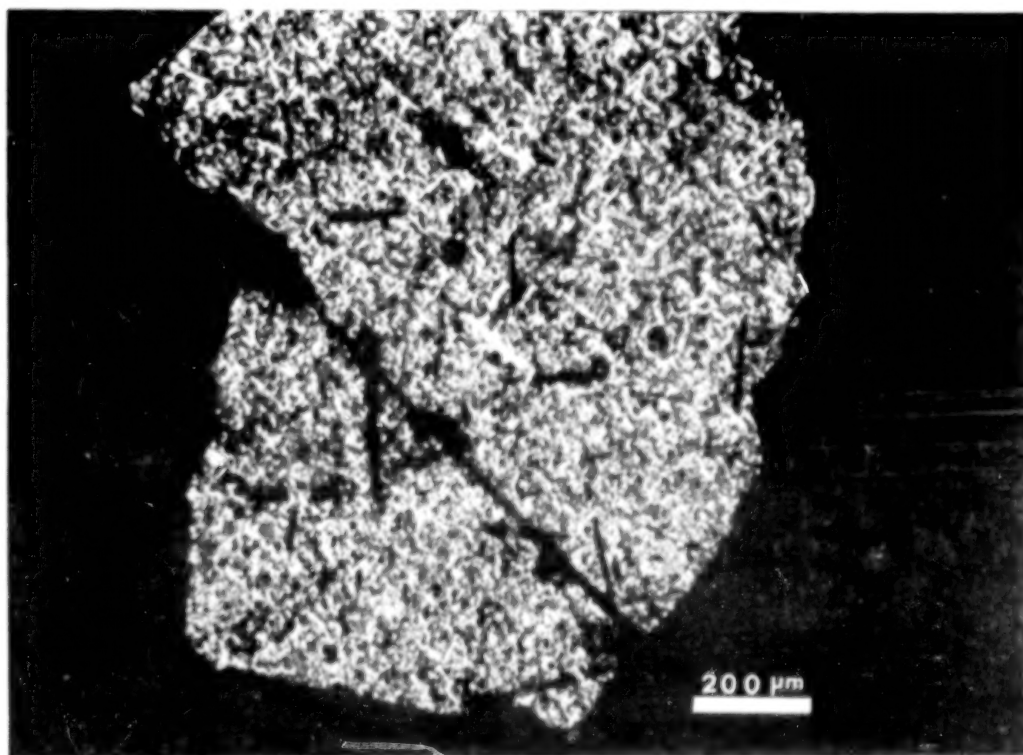


Figure 4. - SASC; 2100-hr exposure at 1370 °C; crossed Nichols. 95X.

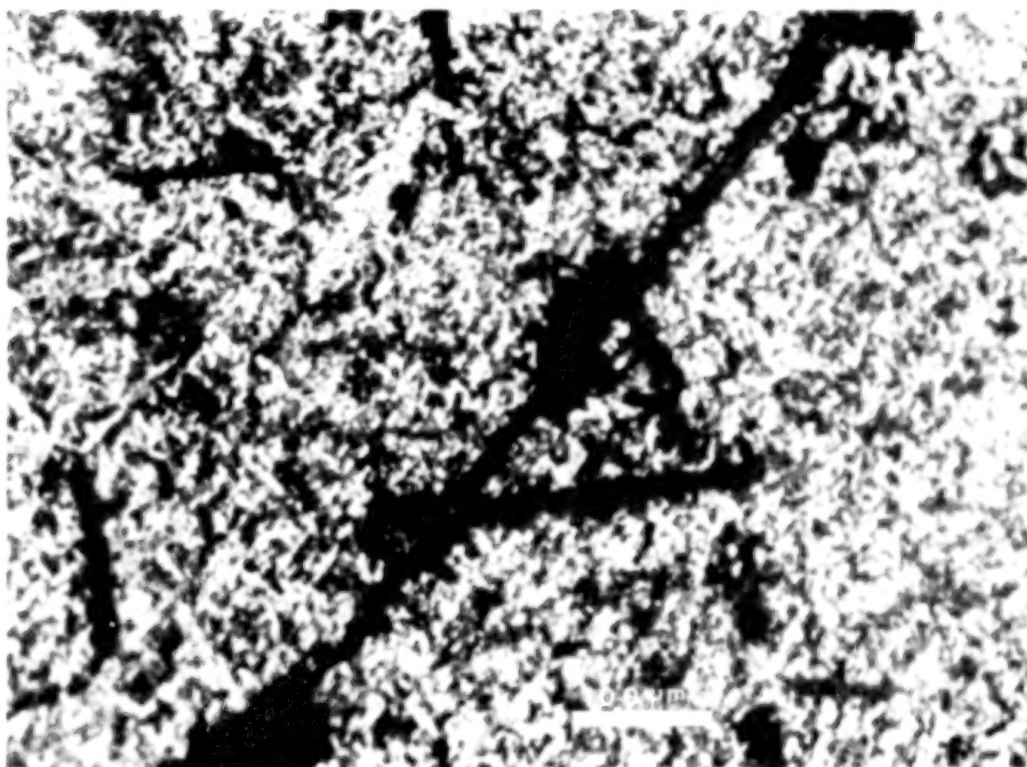


Figure 5. - Same field as fig. 4. 240X.

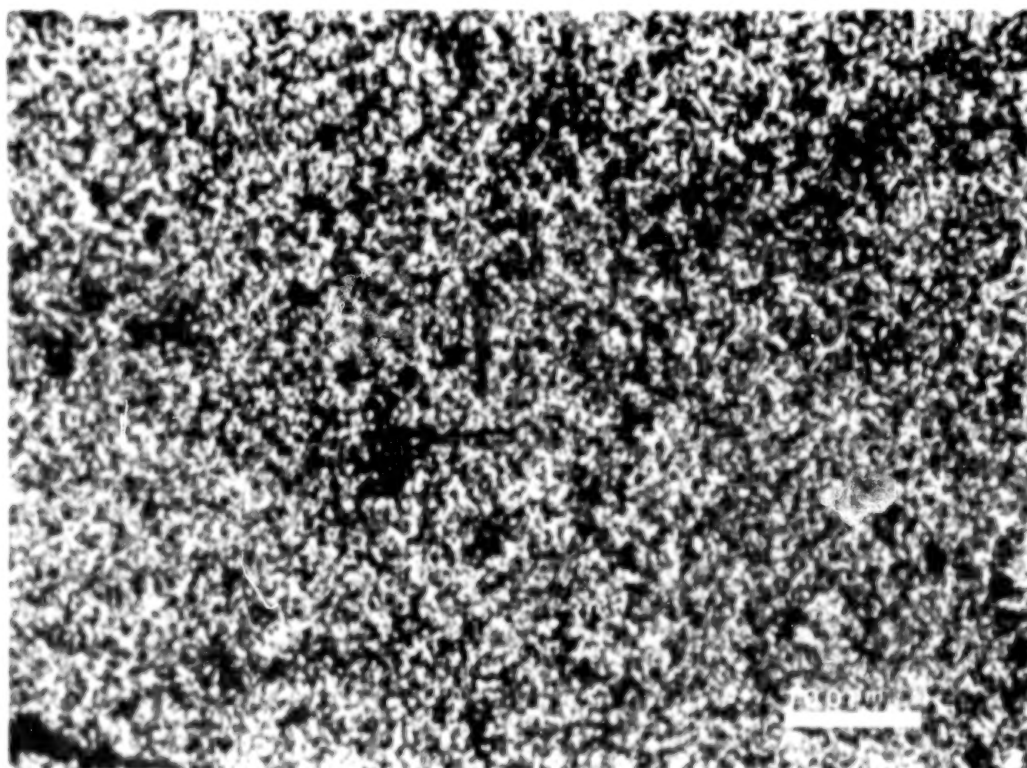


Figure 6. - SASC; 3500-hr exposure at 1370 °C; crossed Nichols. 240X.

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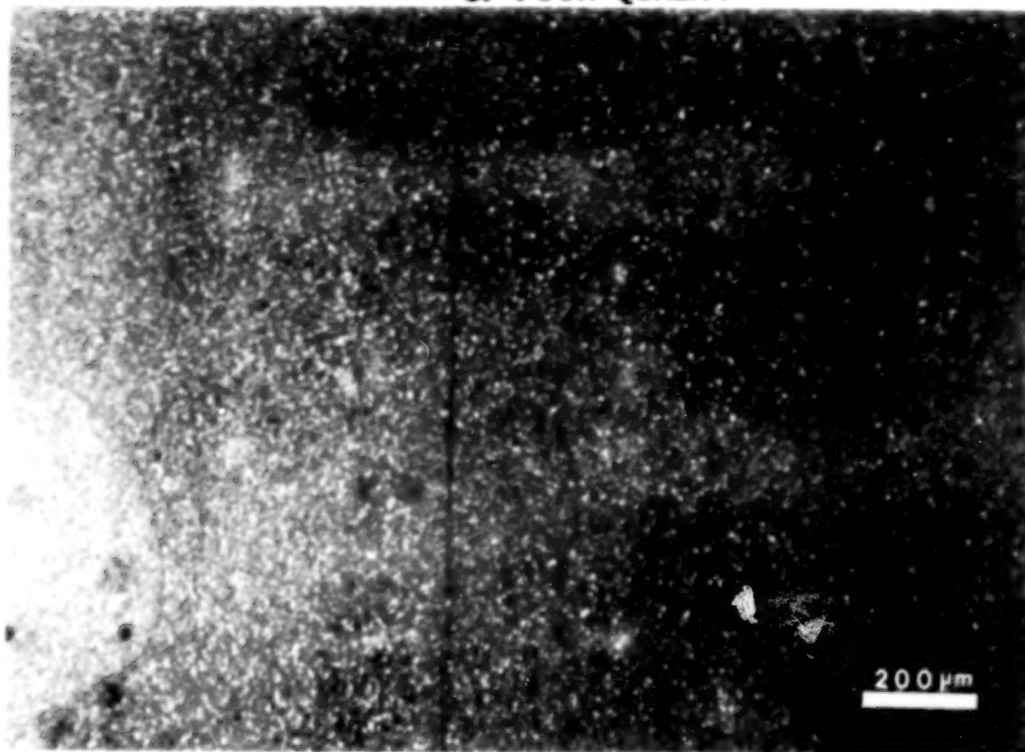


Figure 7. - Baseline Toshiba SSN; crossed Nichols. 95X.

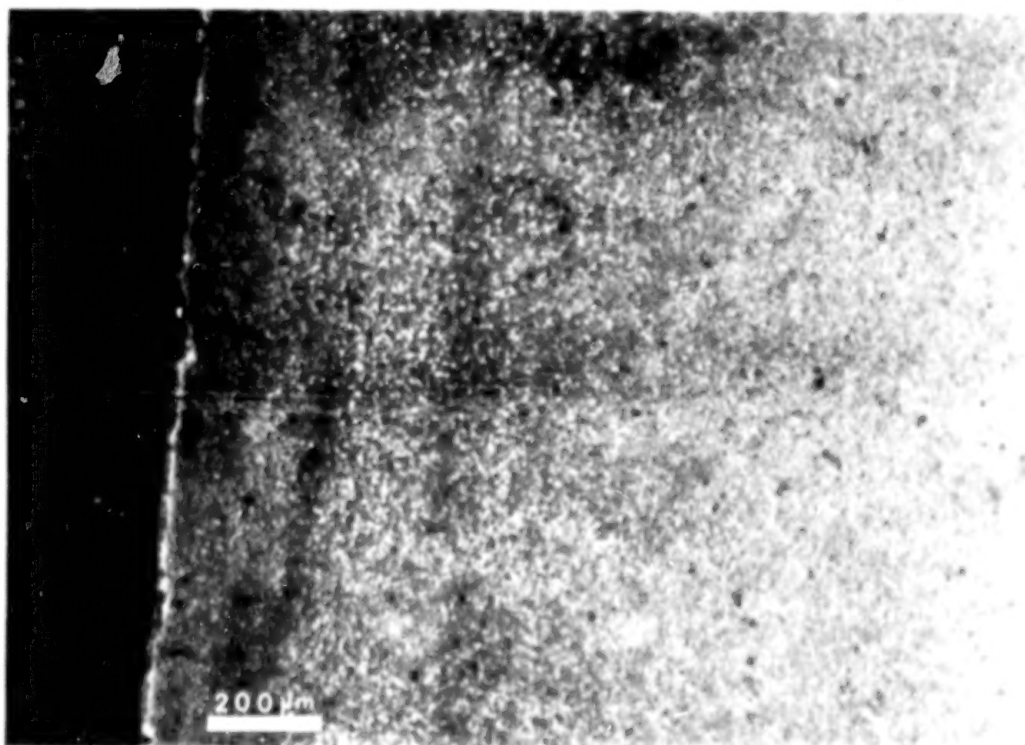


Figure 8. - Toshiba SSN; 350-hr exposure at 1205 °C; crossed Nichols. 95X.

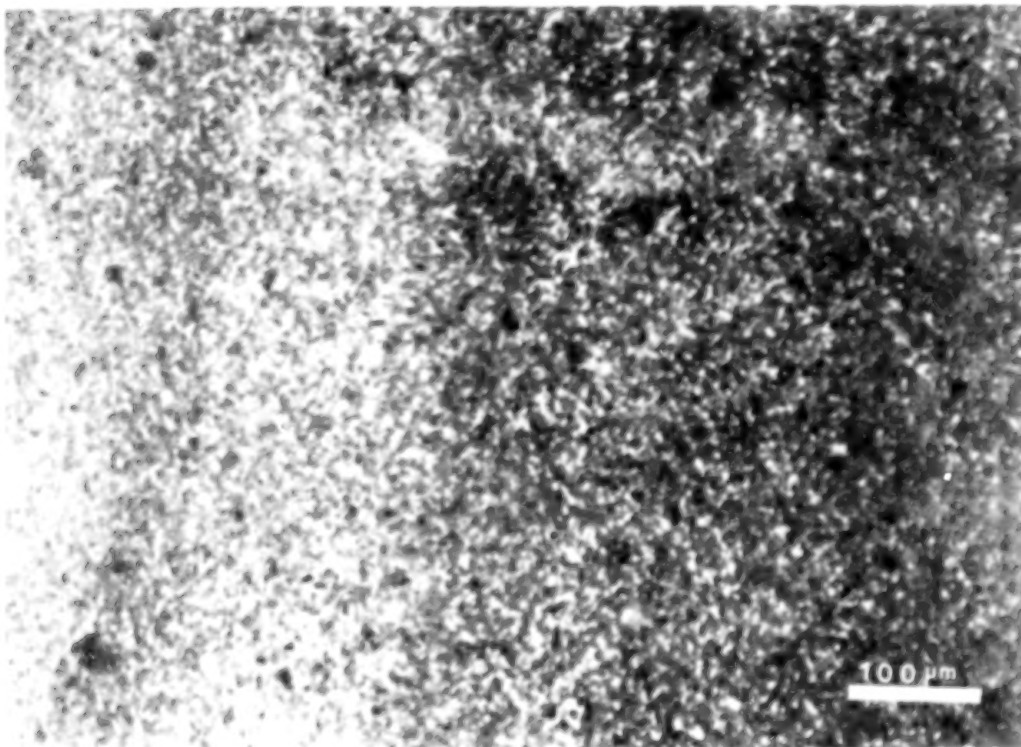


Figure 9. - Same specimen as fig. 8; field near interface; crossed Nichols. 240X

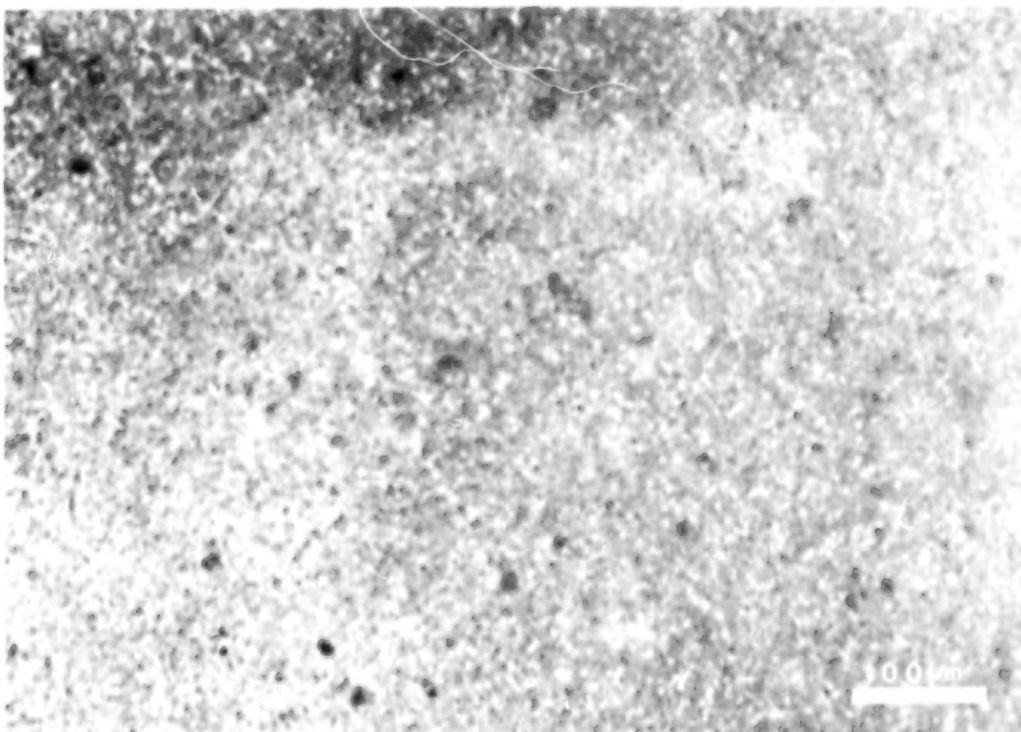


Figure 10. - Same specimen as fig 8; field far from interface; crossed Nichols. 240X.

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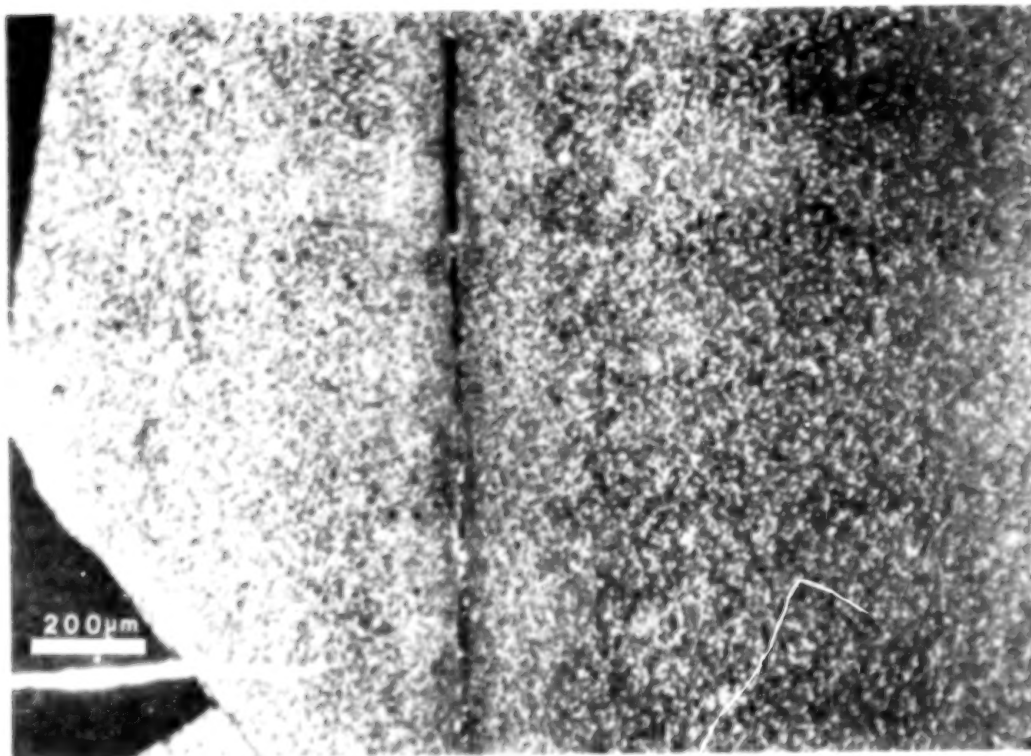


Figure 11. - Toshiba SSN; 700-hr exposure; crossed Nichols. 95X.

N88 - 23888 ^{P.1}

CERAMIC MATRIX COMPOSITES

James A. DiCarlo
NASA Lewis Research Center
Cleveland, Ohio 44135

An overview is presented covering NASA Lewis research efforts aimed at materials and processing development for structurally reliable fiber-reinforced ceramic matrix composites (FRC). With the primary goal of developing technology for strong, tough Si-based FRC with use-temperatures above 1400°C, guidelines for optimum material properties and current problems in achieving these properties are discussed. Brief descriptions of particular research projects directed toward solving these problems are presented. Particular emphasis is placed on those efforts addressing the critical need of developing high performance SiC fibers with stability above 1400°C and with proper coatings for optimum composite structural performance. Based on current results for fiber and matrix development, concluding remarks are made concerning future directions for NASA Lewis FRC studies.

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CERAMIC MATRIX COMPOSITES

BY

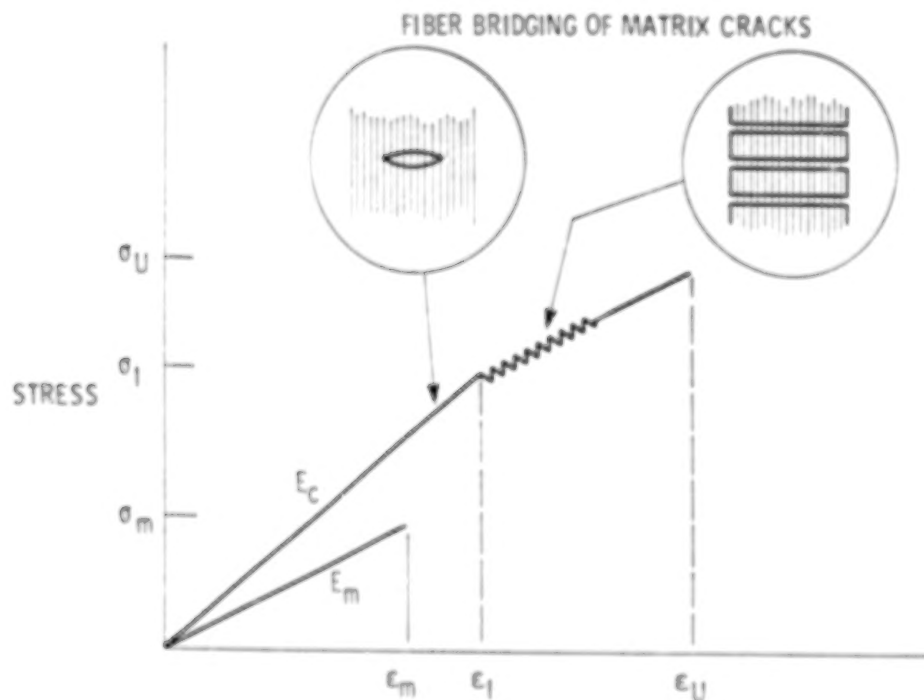
J. DICARLO

DEPUTY CHIEF, CERAMICS BRANCH

OBJECTIVE: TECHNOLOGY DEVELOPMENT FOR FABRICATION OF STRONG, TOUGH, AND RELIABLE CERAMIC COMPOSITES FOR AEROSPACE STRUCTURAL APPLICATIONS TO 1400 °C AND ABOVE

PRIMARY APPROACH: FIBER REINFORCED CERAMICS (FRC) - REINFORCEMENT OF SI-BASED CERAMIC MATRICES WITH CONTINUOUS HIGH PERFORMANCE CERAMIC FIBERS

FRC DEFORMATION AND FRACTURE



CS-84-2357

STRUCTURAL ADVANTAGES OF FIBER REINFORCED CERAMICS

- IMPROVED STIFFNESS
 - MATRIX FRACTURE STRENGTH
 - MATRIX FRACTURE STRAIN
 - FRACTURE TOUGHNESS
 - THERMAL SHOCK
- * METAL-LIKE STRESS-STRAIN BEHAVIOR
- * ULTIMATE FAILURE INDEPENDENT OF MATRIX FRACTURE
- * NONCATASTROPHIC MATERIAL FAILURE

- * AVAILABLE ONLY FOR HIGH ASPECT RATIO REINFORCEMENT

FRC - KEY TECHNICAL ISSUES

I. FABRICATION APPROACH FOR HIGH FRC STRENGTH

- PREPARATION OF OPTIMUM MATRIX PRECURSORS
- UNIFORM PRECURSOR INFILTRATION INTO FIBER ARRAY
- MATRIX CONSOLIDATION AND DENSIFICATION WITHOUT
 - FIBER STRENGTH DEGRADATION
 - LARGE SHRINKAGE CRACKS OR POROSITY
 - NONUNIFORM FIBER DISTRIBUTION

II. AVAILABILITY OF HIGH PERFORMANCE CERAMIC FIBERS

- HIGH STRENGTH AND STIFFNESS
- THERMAL STABILITY ABOVE 1200 °C
- SMALL DIAMETER

III. FIBER COATINGS

- FIBER STRENGTH RETENTION UNDER FRC PROCESSING AND USE
- OPTIMUM FOR COMPOSITE TOUGHNESS AND OFF-AXIS STRENGTH

FRC - CURRENT NASA LEWIS PROGRAMS

I. COMPOSITE FABRICATION

PROCESSING APPROACH	PRIMARY SYSTEM	KEY ISSUES
• REACTION-BONDED Si_3N_4 WITH CVD SIC FIBERS	SIC/RBSN	- STRENGTH AND TOUGHNESS GREATER THAN RBSN - THERMAL STABILITY TO 1400 °C
• CARBON MATRICES REACTION BONDED WITH SILICON	SIC/RBSC	- MATRIX MORPHOLOGY AND SILICONIZATION - FIBER DEGRADATION
• POLYMER-DERIVED PRECURSORS TO SIC AND Si_3N_4 MATRICES		- HIGH CHAR YIELD - INFILTRATION RHEOLOGY WITH CERAMIC FILLERS

FRC - CURRENT NASA LEWIS PROGRAMS

II. HIGH PERFORMANCE SIC FIBERS

- | | |
|---|---|
| • HIGH TEMPERATURE PROPERTIES
OF COMMERCIAL SIC FIBERS | - FIBER PROCESSING APPROACH BEST
SUITED FOR HIGH TEMPERATURE FRC |
| • POST PROCESSING OF NICALON
FIBERS AT HIGH PRESSURE | - POTENTIAL OF HIPPING FOR IMPROVING
NICALON THERMAL STABILITY |

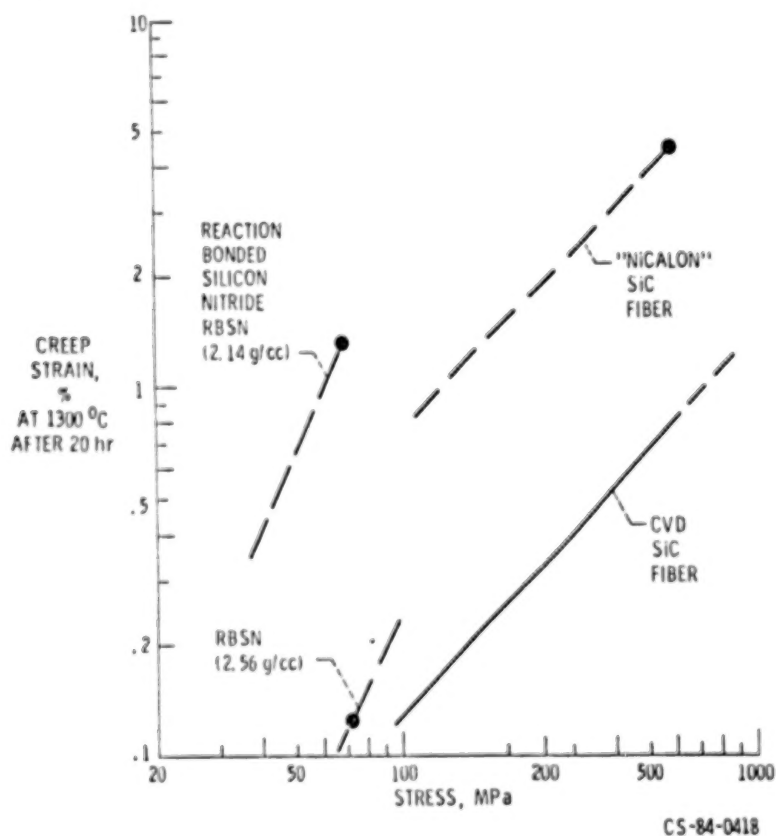
III. FIBER COATINGS

- | | |
|---|--|
| • OXYGEN EFFECTS ON COMMERCIAL
COATINGS FOR CVD SIC FIBERS | - COATING DESIGN FOR OXIDATION
RESISTANCE |
| • FIBER-MATRIX LOAD TRANSFER IN
SIC/RBSN COMPOSITES | - COATING DESIGN FOR COMPOSITE
TOUGHNESS AND STRENGTH |

PROPERTY COMPARISON - COMMERCIAL SiC FIBERS

TYPE:	NICALON (NIPPON CO.)	SCS (AVCO)
PRODUCTION METHOD:	POLYMER SPUN, CURED, PYROLYZED	CVD ONTO CARBON FILAMENT (1300 °C)
FORM:	MULTIFILAMENT YARN (500 PER TOW)	MONOFILAMENT
DIAMETER, μm :	10 TO 20	142
MODULUS, GPa:	180	390
STRENGTH, GPa:		
20 °C:	2.0	>3.5
1400 °C:	<1.0	>2.5

CVD SiC FIBERS PROVIDE CREEP RESISTANCE TO RBSN MATRICES



ADVANTAGES OF FIBER COATINGS FOR CERAMIC MATRIX COMPOSITES

PHYSICAL - CHEMICAL:

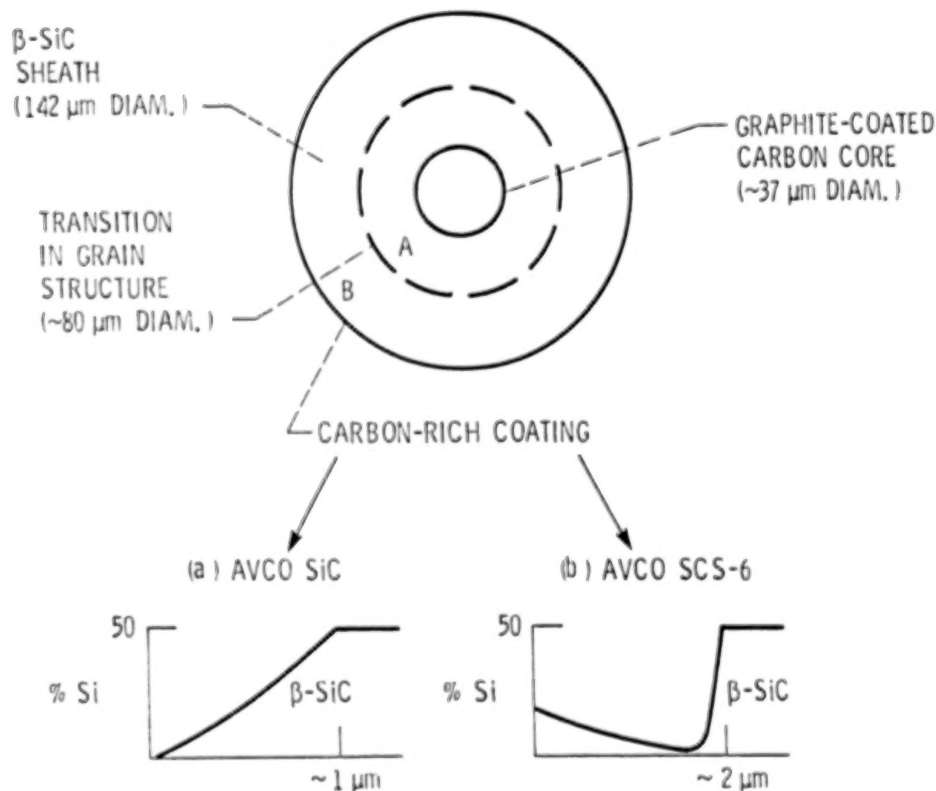
- CAN SERVE AS A DIFFUSION BARRIER INHIBITING INTERDIFFUSION AND REACTIONS WITH MATRIX AND AGGRESSIVE GASES, SUCH AS, OXYGEN
- MINIMIZE DEGRADATION OF FIBER STRENGTH AND FIBER - MATRIX INTERFACIAL BONDING

STRUCTURAL:

- REDUCE MECHANICAL DEGRADATION DURING HANDLING AND COMPOSITE PROCESSING
- REDUCE INTERNAL DEGRADATION BY TRAPPING EVOLVING GASES
- HEAL FIBER SURFACE FLAWS AND INCREASE FIBER STRENGTH
- PROVIDE WEAK FIBER - MATRIX BONDING FOR CRACK DEFLECTION AND TOUGH COMPOSITES

CS-85-0274

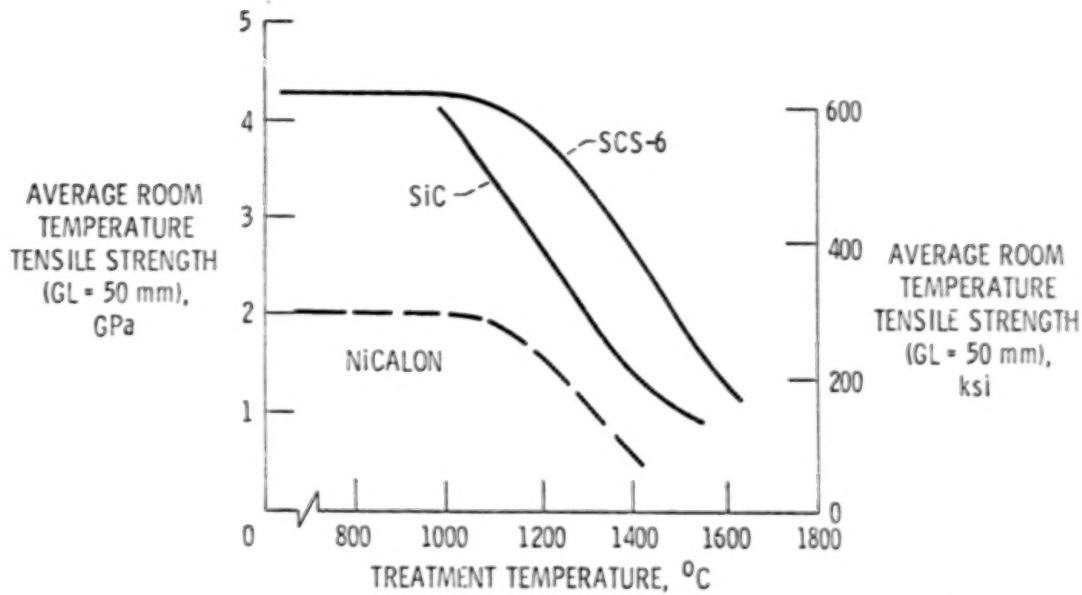
CVD SiC FIBER CROSS SECTION AND COATINGS



CS-84-0419

STRENGTH RETENTION OF SiC FIBERS

ARGON OR NITROGEN, 15 min (10^{-4} ATM OXYGEN)



CS-84-2355

CERAMIC COMPOSITES - FUTURE DIRECTIONS

I. FRC FABRICATION

- SiC/RBSN OPTIMIZATION
- CVD-CVI PROCESSING
- COMBINED PROCESSING APPROACHES
- TOUGHENING ADDITIONS TO MATRIX
- MULTITYPE FIBERS AND FIBER WEAVES
- HYBRID MATRICES

II. HIGH PERFORMANCE CERAMIC FIBERS

- MULTIFILAMENT TOW OF SMALL DIAMETER CVD SiC FIBERS
- SINGLE CRYSTAL SiC AND OXIDE FIBERS
- NEW INNOVATIVE PROCESSING

III. FIBER COATINGS

- STABLE AND OPTIMIZED CVD SiC-C COATINGS
- OTHER CERAMIC COATINGS BY CVD, SOL-GEL, ETC

N88-23889

P-9

Polymer Precursors for SiC Ceramic Materials

by

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Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

CH 446724

We have worked on precursor polymers to SiC, concentrating on polymers made from decamethyl cyclohexasilylene units. Our initial approach was to synthesize mixed diphenyl decamethyl cyclohexasilane, dephenylate and polymerize. This produced polymers which had yields of up to 50% SiC. [Theoretical yield is 75%.] Our present approach is to make polymer through the intermediate trans-1,4-diphenyl decamethyl cyclohexasilane. This should produce a crystalline polymer and high strength fibers. These will be thermally decomposed to SiC fibers. This requires new chemistry which we are studying now.

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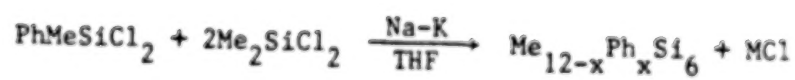
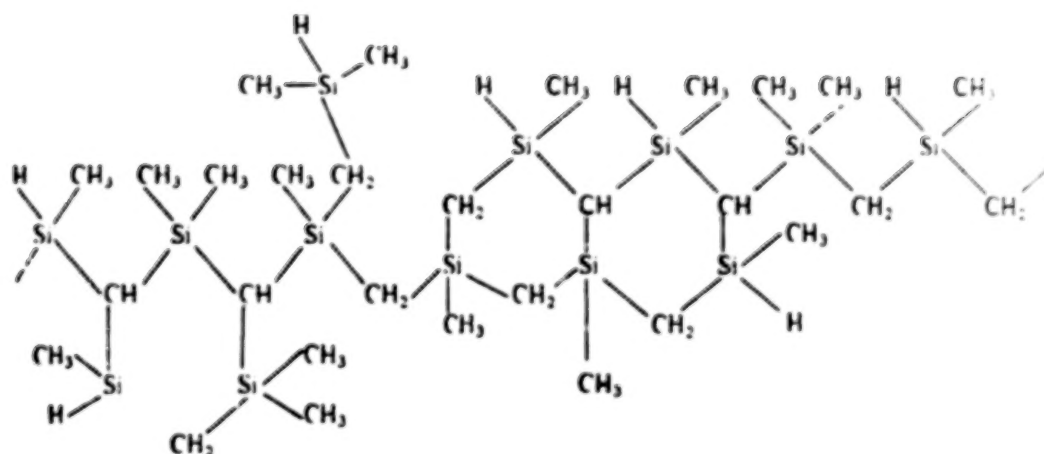
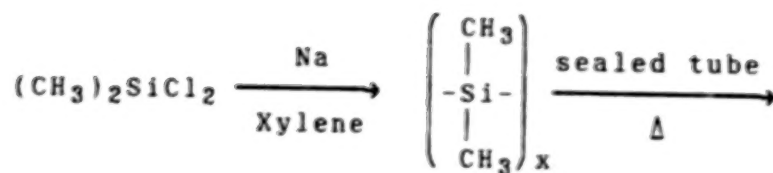


TABLE 1. PERCENT YIELD OF VARIOUS ISOLATED DERIVATIVES

$\frac{\text{Me}}{12-x} \frac{\text{Ph}}{x} \text{Si}_6$	wt(%)	Yield	
		mol(%)	mol(%) (theoretical)
0	8	11	8.8
1	24	27	26.3
2	32	32	32.9
3	36	30	21.9
4			8.2
5			1.6
6			0.1

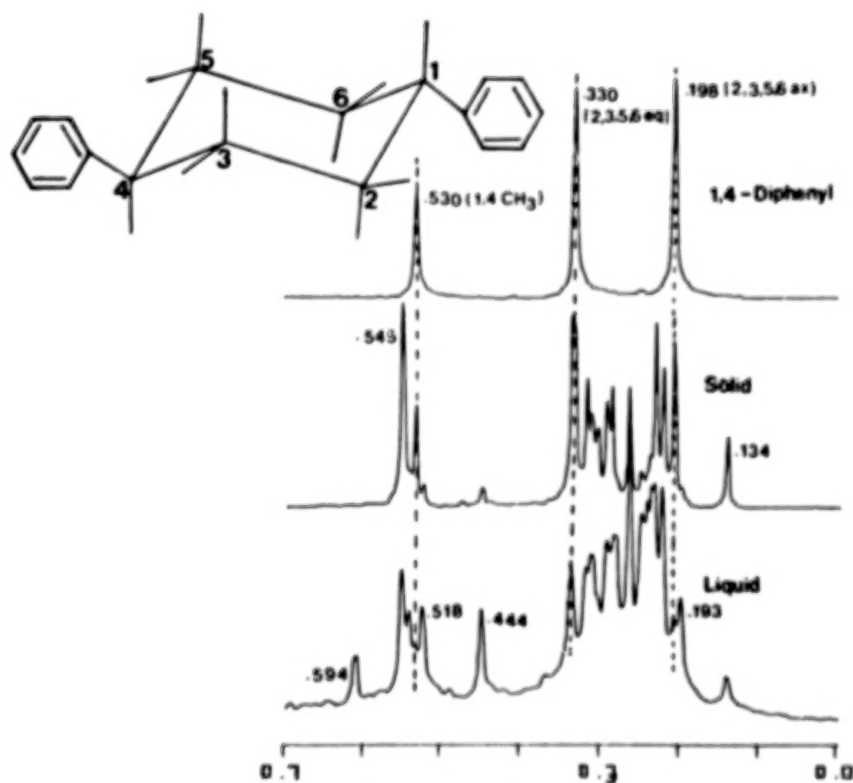


FIG 1. NMR OF DIPHENYLDECAMETHYLCYCLOHEXASILANE

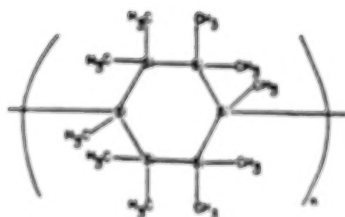
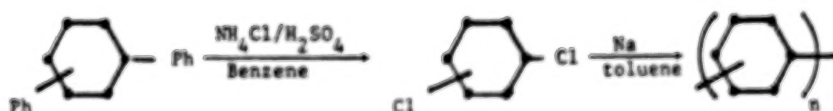
TABLE 2. ^1H -, ^{13}C -, AND ^{29}Si -NMR CHEMICAL SHIFTS FOR PURE 1,4-DIPHENYLDECAMETHYLCYCLOHEXASILANE

^1H (No. of Methyl Groups) (δ ppm) ^a	^{13}C (No. of Carbon) (δ ppm) ^b	^{29}Si (No. of Silicon) (δ ppm) ^c
0.530 (2)	-4.32 (4)	-41.08 (4)
0.330 (4)	-6.49 (2)	-41.40 (2)
0.198 (4)	-6.71 (4)	
	134.68 (o,4)	
	127.86 (p,2)	
	127.71 (m,4)	
	146.98 (1,2)	

a - CH_2Cl_2 (δ 5.35) was used as an internal reference.

b - CDCl_3 (δ 77.0) was used as an internal reference.

c - TMS (δ 0.0) was used as an internal reference.



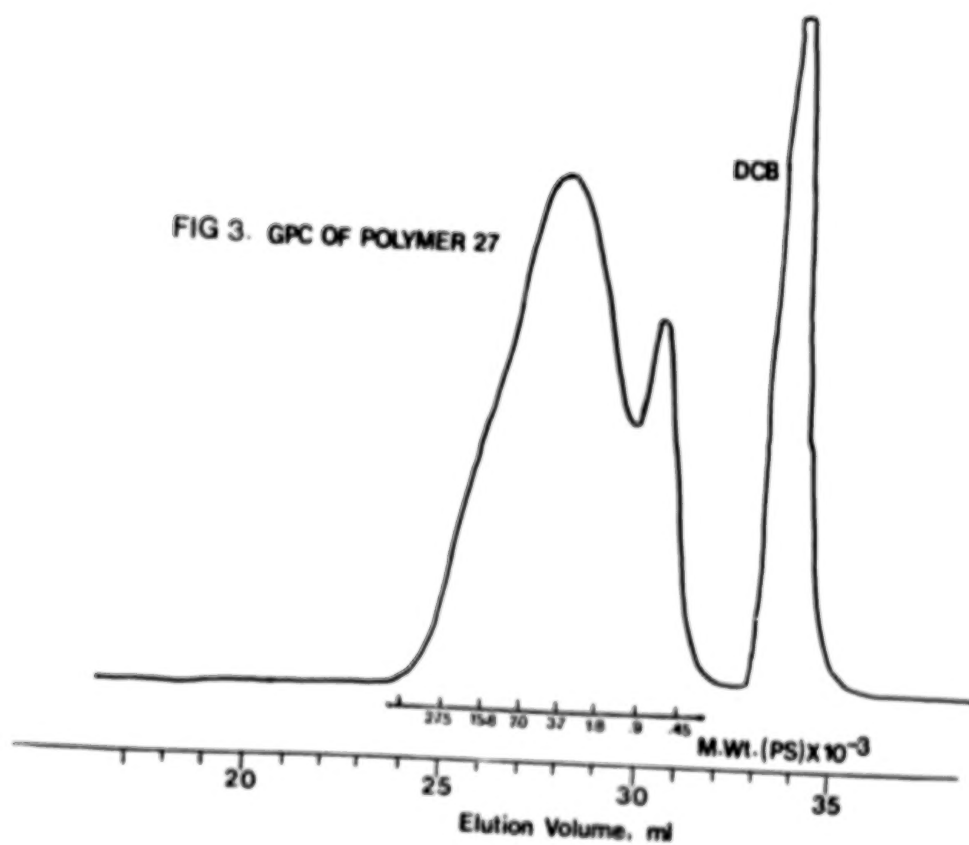
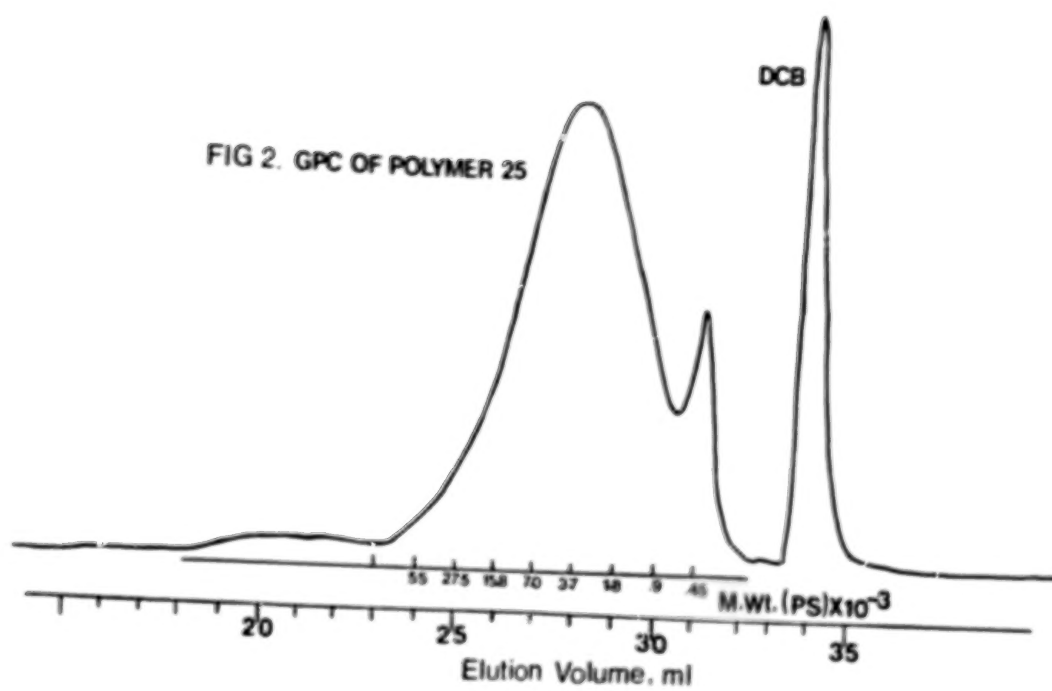


TABLE 1 ELEMENTAL ANALYSIS OF POLYMER25 AND POLYMER27

Polymer	Analytical	% C	% H	% Si	% O
Polymer25	Calcd.:	37.74	9.43	52.83	0
	Found:	33.52	8.69	48.22	9.57 (by difference)
Repeat	Found:	34.40	8.51	-----	None or Trace
Polymer27	Calcd.:	37.74	9.43	52.83	0
	Found:	38.10	9.65	48.70	3.55 (by difference)
Repeat	Found:	40.14	9.23	-----	0.16

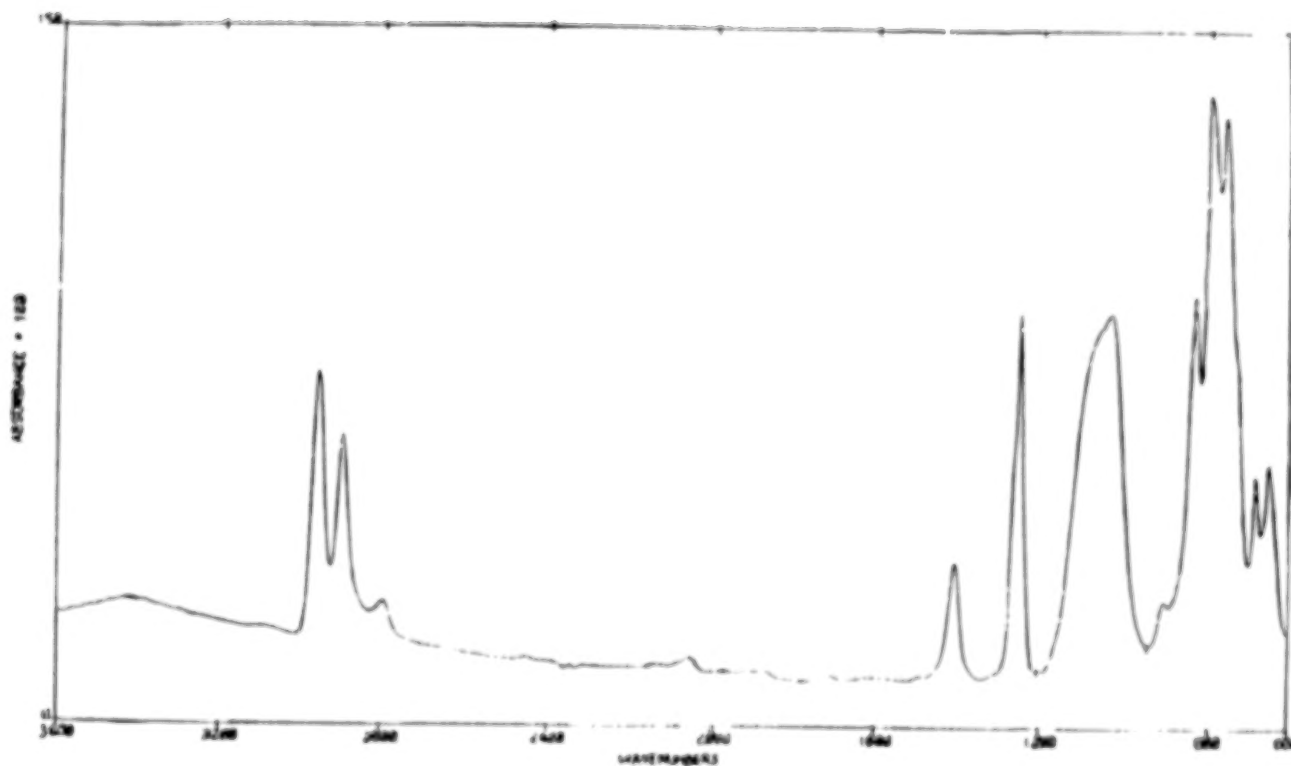


FIG 6. IR OF POLYMER25

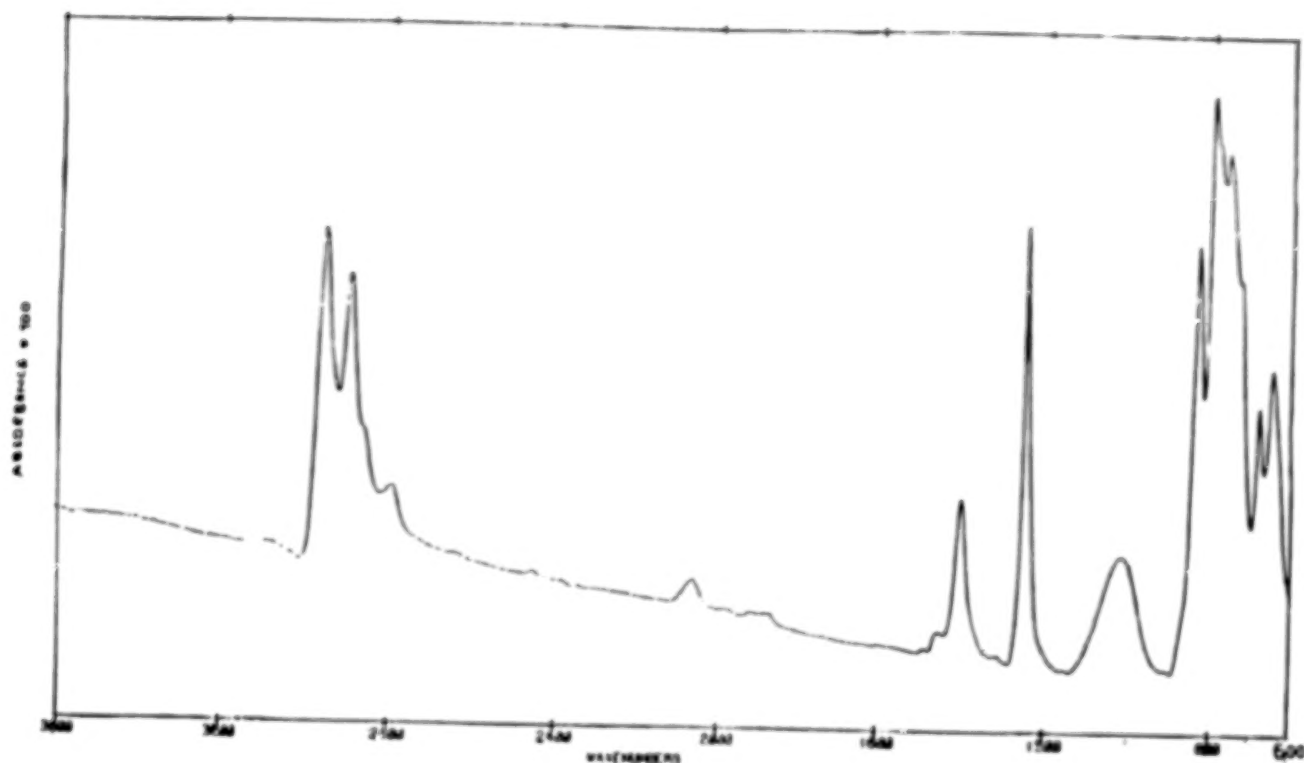


FIG 7. IR OF POLYMER27

TABLE 2 THERMOGRAVIMETRIC ANALYSIS OF POLYMER25 CURED AT VARIOUS TEMPERATURES

Temperature/Time	Char Yield %	Heating Rate
Polymer25	27.39	1.5°C/min
124° ± 4°C/4 hrs (a)	18.75	10° C/min
200° ± 1°C/5 min	20.85	10° C/min
250° ± 5°C/15 min	(a) 20.80	10° C/min
	(b) 48.27	10° C/min
200° ± 1°C/5 hrs	(c) 51.52	10° C/min
	17.74	10° C/min
	36.47	10° C/min
	25.71	15° C/min
	19.64	1.5°C/min

(a) Hexane soluble fraction (59.8% of total polymer).

(b) Gel (12.67% of the total polymer).

(c) A piece of polymer was used, rather than ground powder.

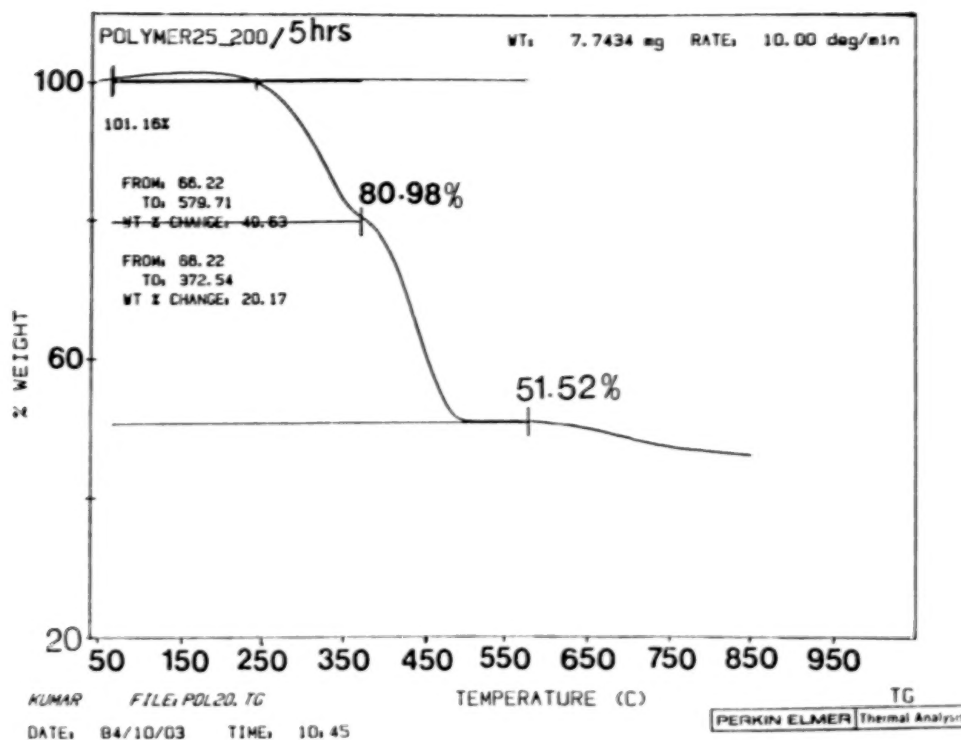
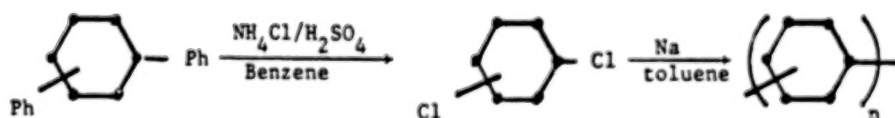


FIG 8.TGA

New Work

Trans-1,4-diphenyl decamethyl cyclohexasilane

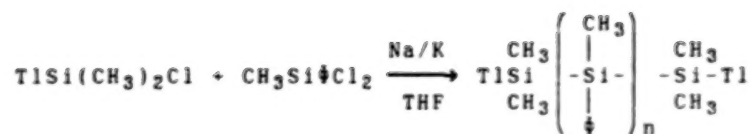
mp = 169.5-170°C, yield = 0.2%



Poly(trans 1,4^l-decamethyl cyclohexasilane)

1. Crystallizable polymer.
2. Should be spinnable from solvent in nematic form.
3. Strong, stable fiber
4. Could retain strength to some degree during pyrolysis to SiC.
5. Higher yield and easier processing than present materials.

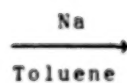
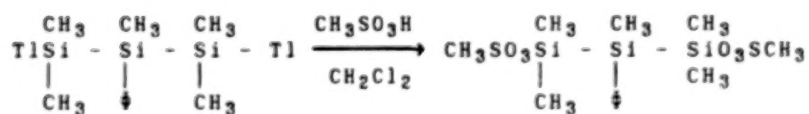
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Tl = p-Tolyl n = 0 → ?

Theory - highest yield = 27% of n=1

Best yield so far = 20%, n=0,1,2,3,4 isolated



N88-23890 ^{P-4}

POLYMER PRECURSORS FOR CERAMIC COMPOSITES

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Cleveland, Ohio 44135

The fiber composite approach to reinforced ceramics provides the possibility of achieving ceramics with high fracture toughness relative to monolithics. Fabrication of ceramic composites, however, demands low processing temperatures to avoid fiber degradation. Formation of complex shapes further requires small diameter fibers as well as techniques for infiltrating the matrix between fibers.

Polymers offer low temperature processability, control of rheology not available with ceramic powders, and could serve as precursors to fibers of matrix. In recent years, a number of polysilanes and polysiloxanes have been investigated as potential precursors. A review of candidate polymers will be presented, including recent studies of silsesquioxanes underway at LeRC.

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NEEDS

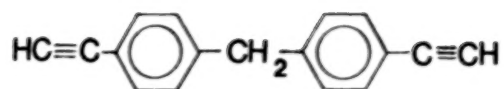
- SMALL DIAMETER CERAMIC FIBER
- HIGH TEMPERATURE, ENVIRONMENTALLY RESISTANT MATRIX

PROBLEMS

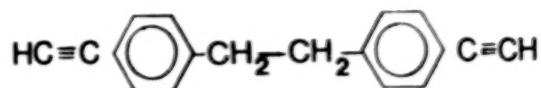
- LOW CHAR YIELD
- HIGH SHRINKAGES - VOIDS
- NEED FOR REPEATED IMPREGNATION
- DEVIATION FROM STOICHIOMETRY - CHEMICAL INSTABILITY AT HIGH TEMPERATURES



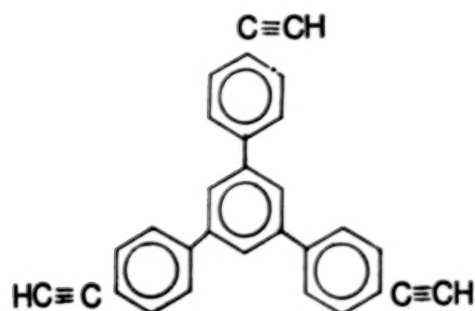
MONOMERS



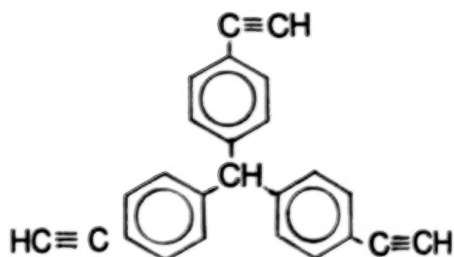
DEDPM
diethynyldiphenylmethane



DEDPE
diethynyldiphenylethane

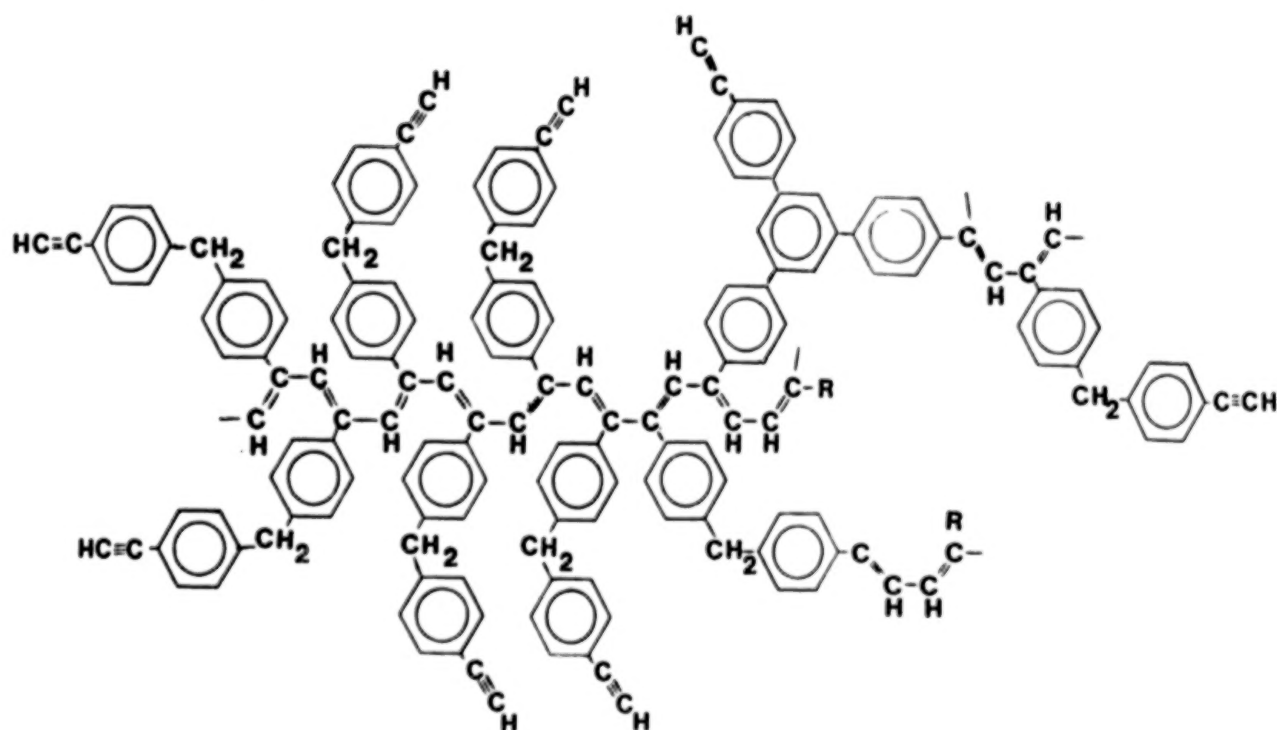


TETPB
triethynyltriphenylbenzene



TETPM
triethynyltriphenylmethane

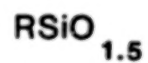
CROSSLINKED HOMOPOLYMER OR COPOLYMER



Si CONTAINING POLYMERS

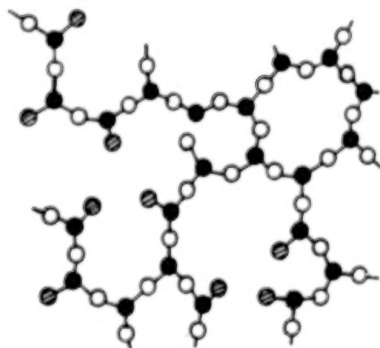
$(\text{CH}_3)_x\text{Si}_y$	METHYLPOLYSILANE
$((\text{CH}_3)_2\text{SiCH}_2\text{SiHCH}_3)_x$	POLYCARBOSILANE
$(\text{C}_6\text{H}_5\text{CH}_2\text{Si})_x((\text{CH}_3)_2\text{Si})_y$	POLYSILASTYRENE
$(\text{CH}_3\text{Si})_x(\text{CH}_2\text{CHSiCH}_3)_y$	VINYLSILANE
$(\text{CH}_3\text{HSiN})_x$	POLYMETHYLSILAZANE
$(\text{CH}_3\text{Si})_x(\text{NCH}_3)_y(\text{NHCH}_3)_z$	POLYCARBOSILAZANE
$\left(\begin{array}{c} \text{Si} - \text{Si} \\ \quad \\ -\text{Si} \quad \text{Si}- \\ \quad \\ \text{Si} - \text{Si} \end{array} \right)_x$	POLY (CYCLOHEXAMETHYLSILANE)

SILSESQUIOXANES

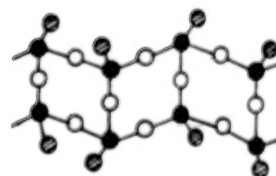


R = methyl, propyl, vinyl, phenyl

T Resin



Ladder Polymer



N88-23891 ^{P. 10}

SiC FIBER ANALYSIS

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NASA Lewis Research Center
Cleveland, Ohio 44135

Polymer derived Nicalon SiC fibers are known to be thermally unstable at temperatures beyond 1200°C. In an effort to further understand the mechanisms of fiber degradation, Nicalon fibers were heat treated at temperatures up to 2200°C and argon gas pressures varying from 0 to 1360 atm. The effects of gas pressure on the thermal stability of the fibers were determined through property comparisons between the pressure-treated fibers and vacuum-treated fibers. Investigation of the thermal stability included studies of the fiber microstructure and mechanical and physical properties before and after treatments.

Nicalon Fiber Thermal Stability

Problem:

- Polymer derived Nicalon SiC fibers degrade significantly in tensile strength above 1200 C in inert environments

Probable Mechanisms:

- Creation of increased internal porosity and flaw growth caused by reactions between SiC, SiO₂, C, and Si₃N₄ in the as-produced fiber
- Grain growth of microcrystalline SiC

Objectives

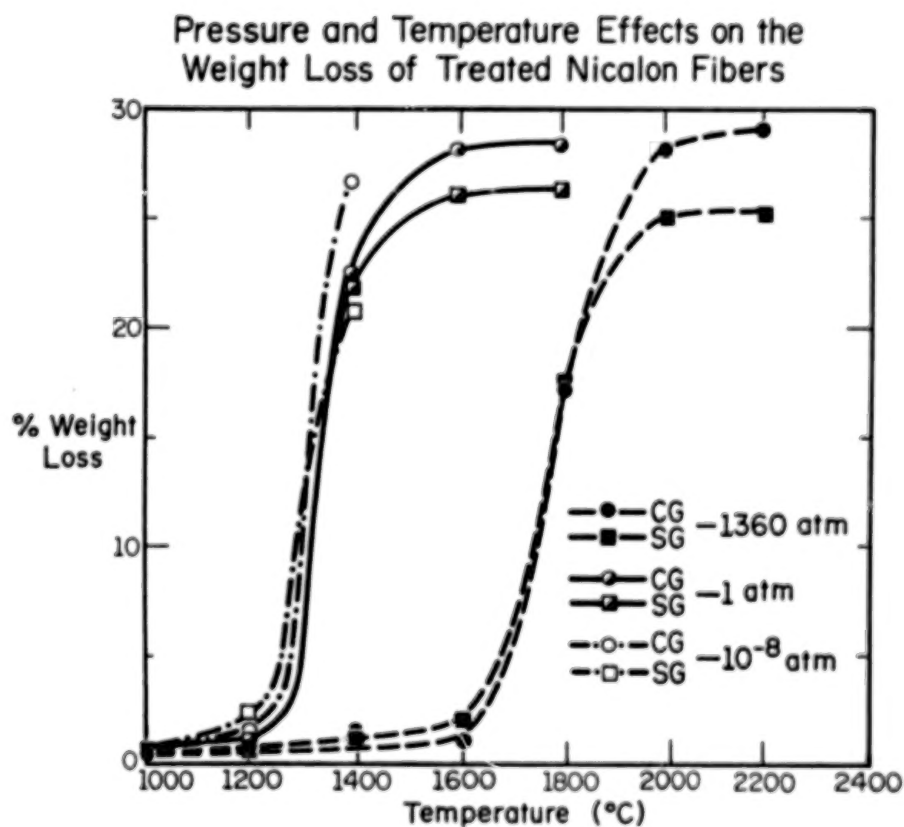
- To determine the effects of heat treatment in high pressure argon on the tensile strength and physical properties of commercially available Nicalon SiC fibers
- To determine whether Hot Isostatic Pressing can offer a viable approach to improving the thermal stability of Nicalon fibers

Experimental Parameters

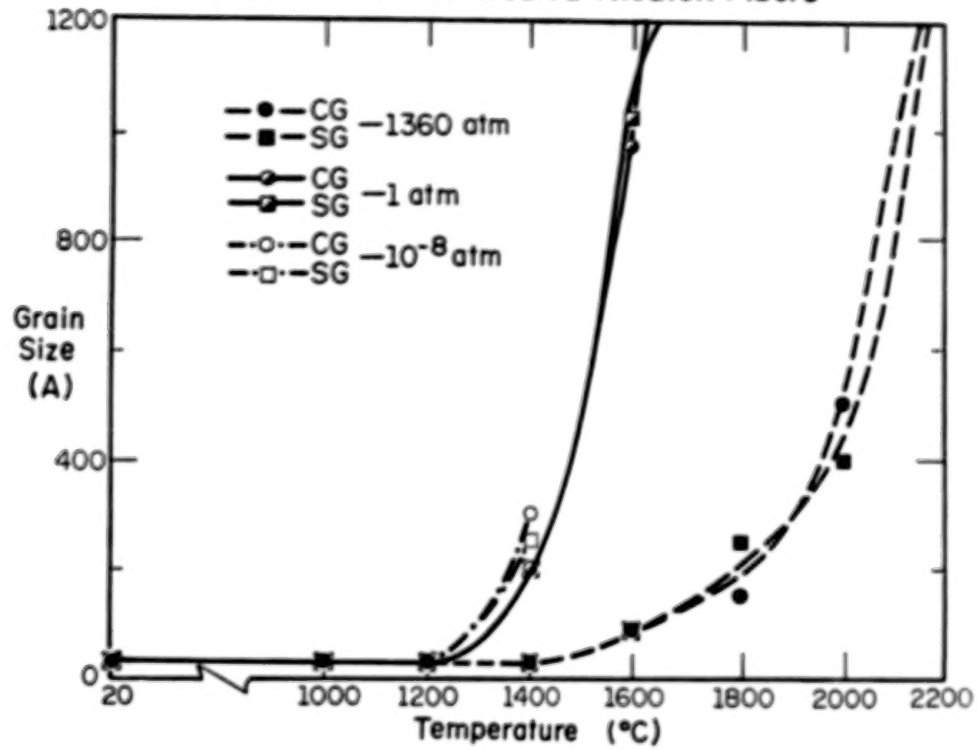
		Si	C	O	N	
Nicalon Fibers:	Ceramic Grade ~40	50	8	2	at%	
	Standard Grade ~37	46	15	2	at%	

Treatment Conditions: Pressure: 10⁻¹, 10⁻⁸, 1360 atm Argon
 Temperature: 1000 - 2200 C
 Time: 1 hour

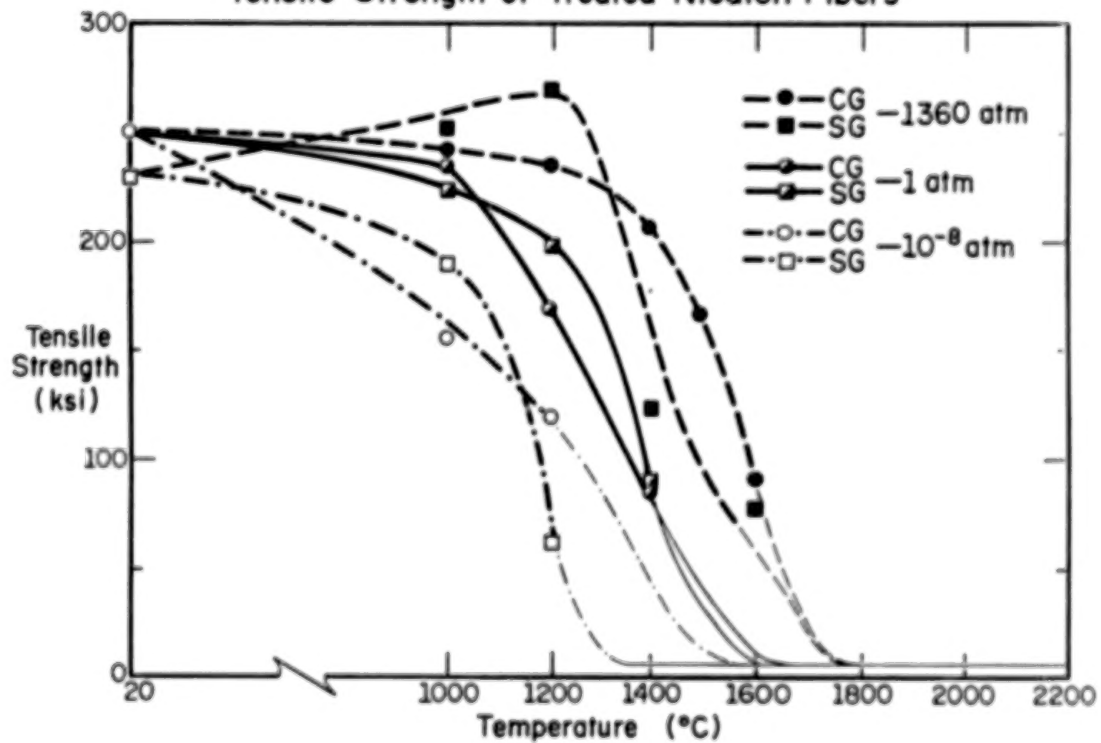
Properties: Weight Loss
 Tensile Strength
 Grain Size
 Microstructure
 Crystalline Phases



Pressure and Temperature Effects on the Grain Growth of Treated Nicalon Fibers



Pressure and Temperature Effects on the Tensile Strength of Treated Nicalon Fibers



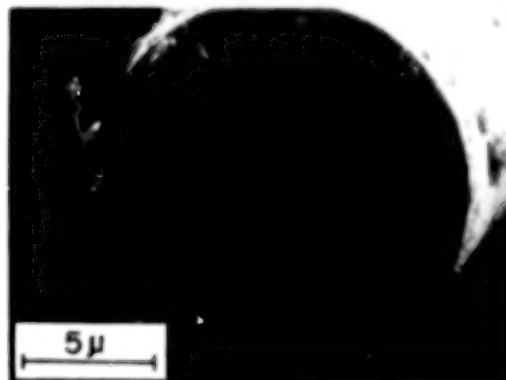
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Fracture Surfaces of As-Received Nicalon Fibers

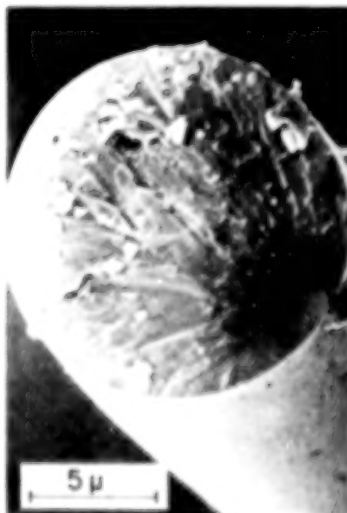
Standard
Grade
250 ksi



Ceramic
Grade
231 ksi



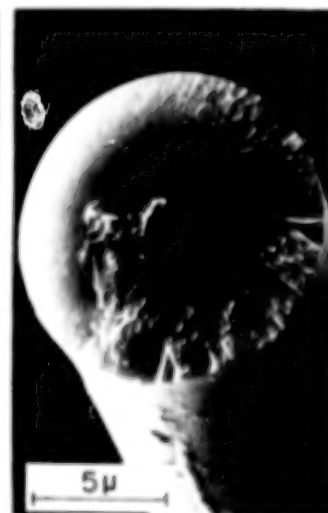
Ceramic Grade Nicalon Heated to 1000 °C



1360 atm
0.6 % wt loss
240 ksi

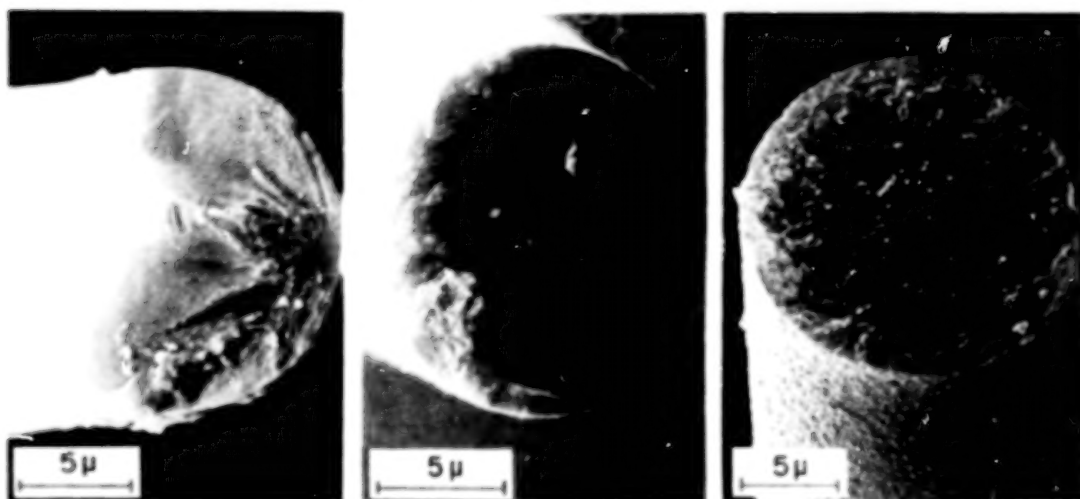


1 atm
0.8 % wt loss
235 ksi



10^{-8} atm
0.8 % wt loss
154 ksi

Ceramic Grade Nicalon Heated to 1400 °C



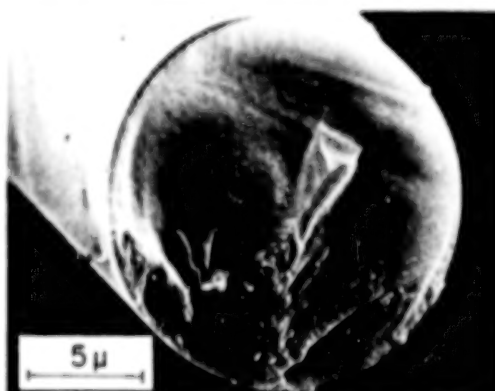
1360 atm
1.0 % wt loss
208 ksi

1 atm
22 % wt loss
85 ksi

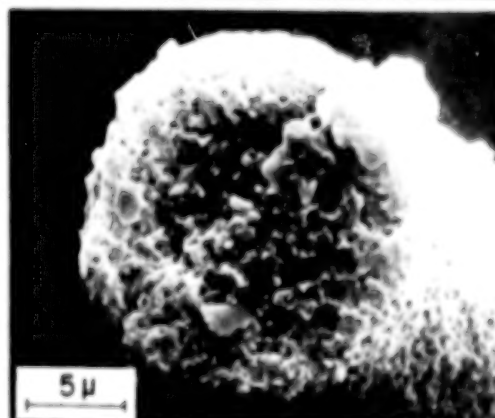
10⁻⁸ atm
27 % wt loss
— ksi

Ceramic Grade Nicalon Fibers Heated to 1600 °C

1360 atm
0.8 % wt loss
90 ksi



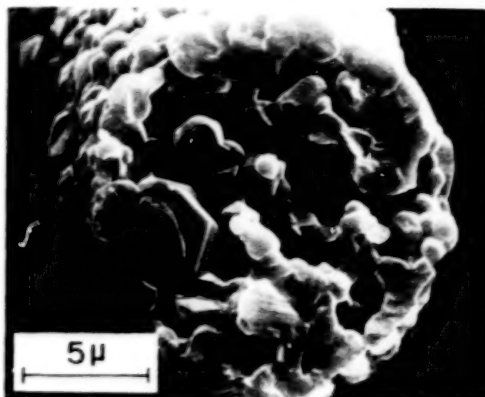
1 atm
28 % wt loss
— ksi



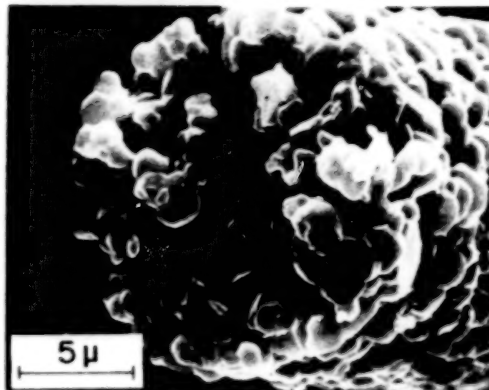
Nicalon Fibers Heated to 2200°C

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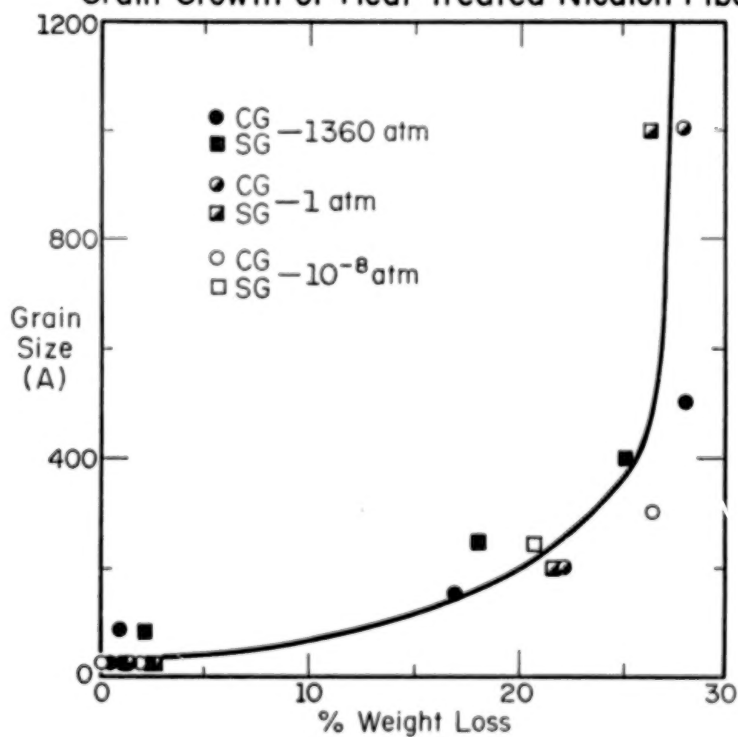
Standard
Grade
1360 atm
25 % wt loss
— ksi

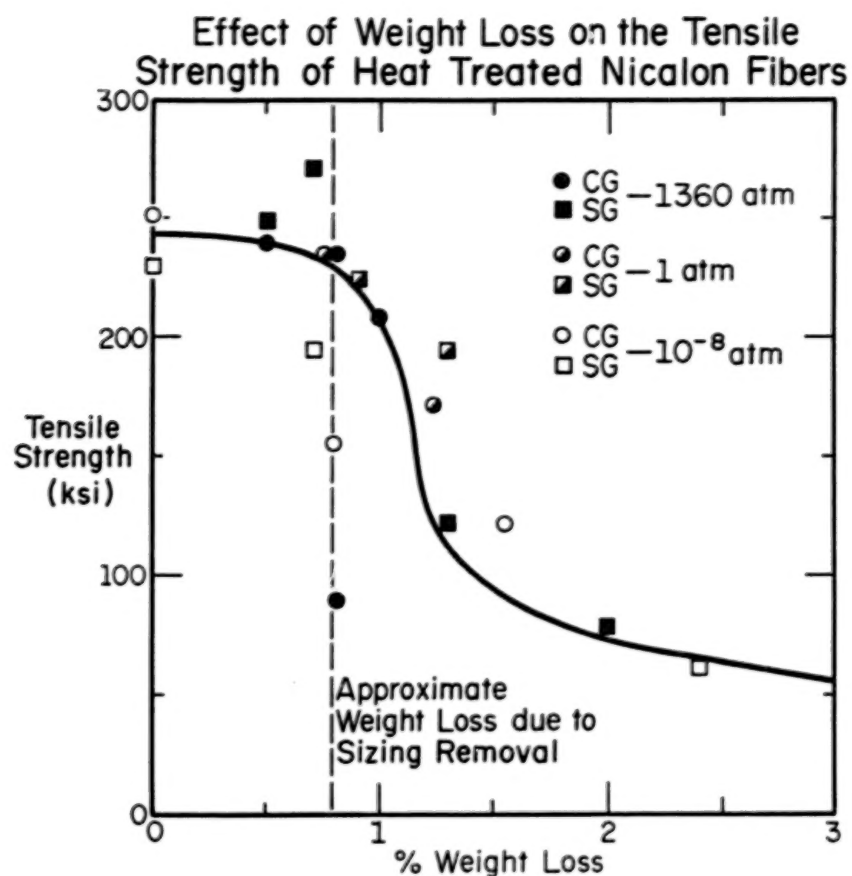


Ceramic
Grade
1360 atm
28 % wt loss
— ksi



Correlation Between Weight Loss and
Grain Growth of Heat Treated Nicalon Fibers





**Results of Additional Heat Treatment Tests
on High Pressure Treated Nicalon Fibers**

Heat Treatment Conditions	% Weight Loss	Tensile Strength (ksi)
	CG / SG	CG / SG
1200 C - 1 hr 1360 atm Ar	0.8 / 0.7	236 / 271
1200 C - 1 hr 1360 atm Ar	28 / 24	-- --
1400 C - 1 hr 1 atm Ar		
1600 C - 1 hr 1360 atm Ar	0.8 / 2.0	90 / 78
1600 C - 1 hr 1360 atm Ar	23 / 26	-- --
1400 C - 1 hr 1 atm Ar		

Pressure Effects on Nicalon Thermal Stability

Summary:

- High pressure treatments in Argon suppress fiber weight loss to temperatures above 1500 C
- Strength degradation and grain growth can be correlated with weight loss and thus are also inhibited by high pressure treatments
- Strength degradation occurs rapidly within the first 1% weight loss (beyond the sizing removal) whereas grain growth does not proceed as rapidly until ~20% weight is reached
- Fibers retreated at 1400 C in 1 atm Ar after high pressure treatment show no improvement in strength over as received fibers treated at 1400 C

Pressure Effects on Nicalon Thermal Stability

Conclusions:

- Increased external pressure creates a diffusion barrier which inhibits CO gas evolution from internal SiO_2 - Carbon reactions thus suppressing fiber weight loss
- Suppression of CO gas evolution may also delay exaggerated grain growth due to the tendency of excess carbon in SiC to act as a grain growth inhibitor
- Initial and major strength degradation mechanism is most likely due to the rapid growth of pre-existing flaws near the surface
- In general, high pressure treatment of commercial Nicalon fibers offers no improvement in thermal stability unless pressure can be maintained throughout composite fabrication and fiber use
- Because of initial porosity and/or creep resistance in the as-produced Nicalon fibers Hot Isostatic Pressing does not appear to be an effective post-fabrication method for improving fiber thermal stability

Fiber Development – Future Directions

Based on potential SiC Properties:

- High modulus (>400 GPa)
- High strength (>4 GPa)
- Creep resistance
- Environmental resistance
- Low density
- High thermal conductivity
- Property retention to above 1400 C

Efforts will continue to develop processing approaches for producing

- Continuous
- Small diameter
- High performance
- Multifilament tows of SiC fibers

Current results indicate CVD Processing as the optimum approach
for the base fibers and for required fiber coatings

SiC FIBER REINFORCED REACTION-BONDED Si_3N_4 COMPOSITES

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NASA Lewis Research Center
Cleveland, Ohio 44135

A technique for fabricating strong and tough SiC fiber reinforced reaction bonded Si_3N_4 matrix composites (SiC/RBSN) has been developed. Using this technique, composites containing ~ 23, 30, and 40 volume fractions of aligned 140 μm diameter, chemically vapor deposited SiC fibers have been fabricated. The room temperature physical and mechanical properties have been evaluated. The results for composite tensile strength, bend strength, and fracture strain indicate that the composite displays excellent properties when compared with the unreinforced matrix of comparable porosity. The composite stress at which the matrix first cracks and the ultimate composite fracture strength increase with increasing volume fraction of fibers, and the composite fails gracefully.

Measurements of room temperature tensile strength of SiC/RBSN composites after 100 hr exposure in flowing air at 1200°C and at 1400°C, and measurements of bend strength at temperatures up to 1300°C did not show any appreciable strength loss from the strength values of as-fabricated composites. The mechanical property data of this ceramic composite are compared with similar data for unreinforced commercially-available Si_3N_4 materials and for SEP SiC/SiC composites.

SIC FIBER REINFORCED REACTION - BONDED Si_3N_4

by

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CLEVELAND, OHIO 44135

OBJECTIVE:

- TO FABRICATE AND EVALUATE PROPERTIES OF FIBER REINFORCED Si_3N_4 MATRIX COMPOSITES FOR ADVANCED HEAT ENGINE APPLICATIONS

RATIONALE:

- Si_3N_4 IS A LIGHT, OXIDATION RESISTANT, THERMAL SHOCK RESISTANT, NONSTRATEGIC MATERIAL BUT LACKS DUCTILITY (TOUGHNESS) AND STRENGTH REPRODUCIBILITY

APPROACH:

- REINFORCEMENT OF Si_3N_4 BY HIGH STRENGTH, HIGH MODULUS CERAMIC FIBER SHOULD
 - IMPROVE TOUGHNESS BY CRACK DEFLECTION AT THE INTERFACE
 - INCREASE FIRST MATRIX FAILURE STRESS DUE TO INCREASE IN STIFFNESS OF MATERIAL

PROPERTIES:

- FIRST MATRIX CRACK STRESS
- ULTIMATE STRENGTH
- INTERFACIAL SHEAR STRENGTH
- THERMAL SHOCK RESISTANCE
- THERMAL STABILITY

TESTS:

- TENSILE STRENGTH - (ROOM TEMPERATURE)
- FLEXURE STRENGTH - (ROOM TEMPERATURE TO 1400 °C)

MATERIALS FOR Si_3N_4 COMPOSITE

FIBERS

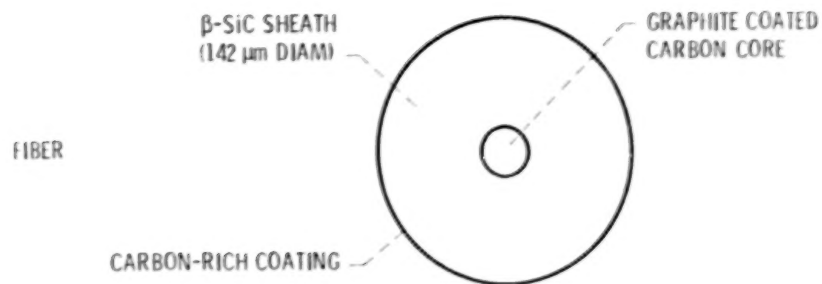
- AVCO CVD SILICON CARBIDE FIBERS
- HIGH MODULUS - 390 GPa (57×10^6 psi)
- HIGH STRENGTH - 3.5 GPa (500 ksi)
- HIGH PURITY
- CREEP RESISTANT
- COMPATIBLE WITH Si_3N_4

MATRIX

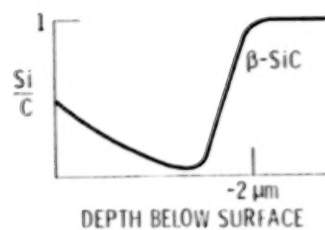
- REACTION-BONDED SILICON NITRIDE
- LOW MODULUS - 100-200 GPa ($15-30 \times 10^6$ psi)
- LOW TEMPERATURE FABRICATION
- NET SHAPE PROCESSING

LD 85 2148

AVCO SiC FIBER COMPOSITION

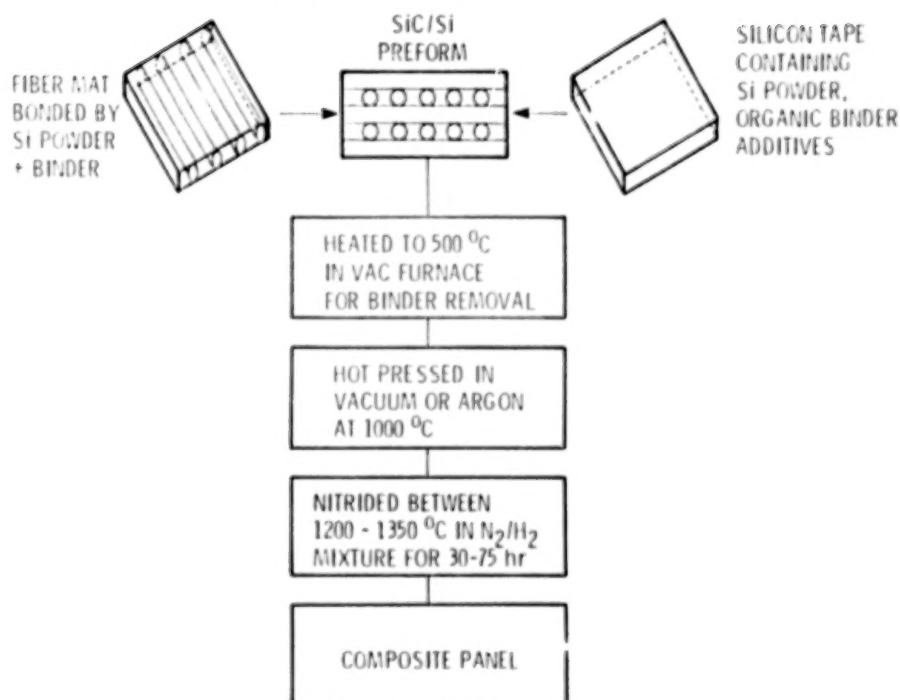


COATING
(SCS-6)



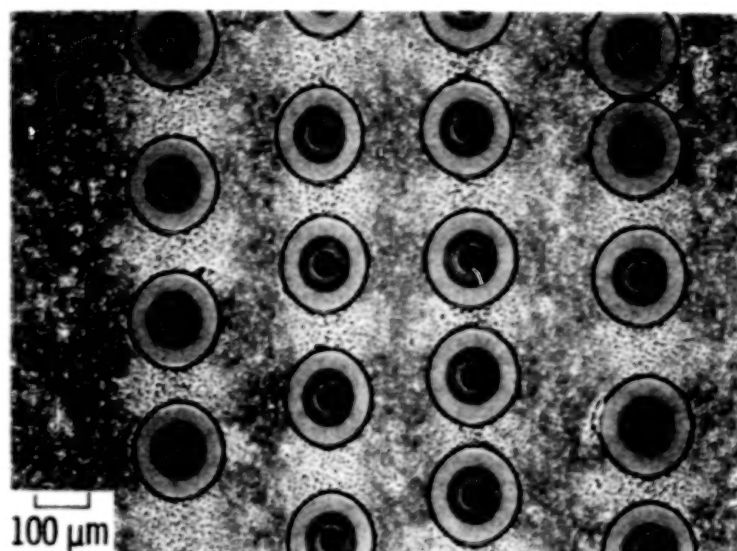
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SiC/RBSN COMPOSITE FABRICATION



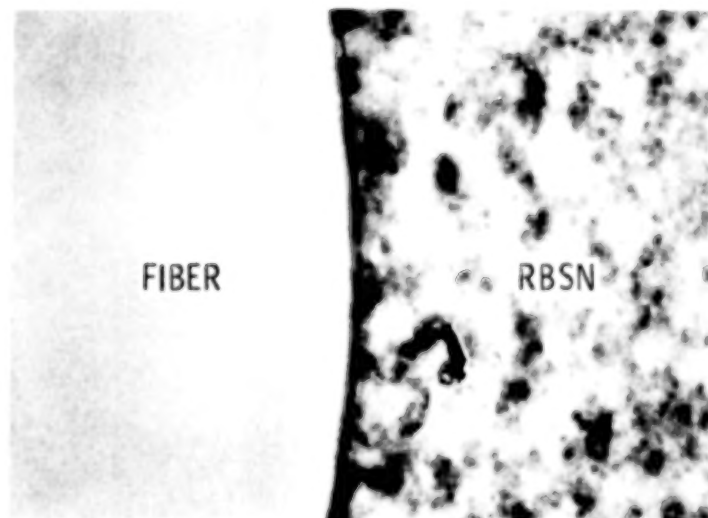
CROSS SECTION OF 39 VOL% SiC/RBSN COMPOSITE

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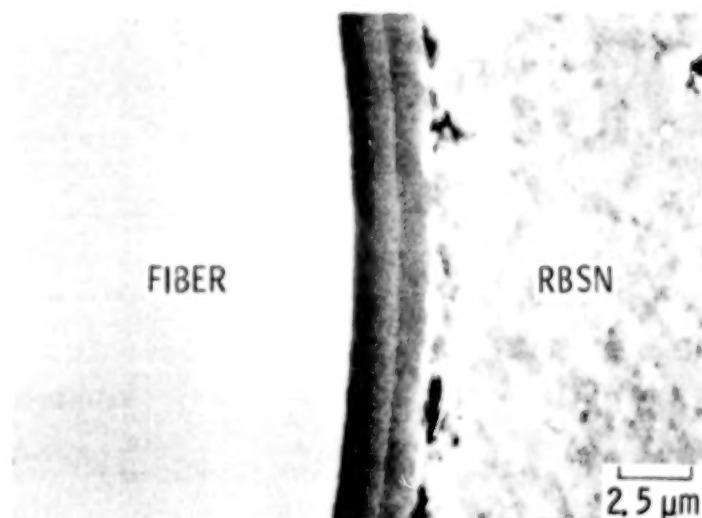


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INTERFACIAL REGION IN SiC/RBSN COMPOSITE



SCS-0 FIBER



SCS-6 (DOUBLE COATED) FIBER

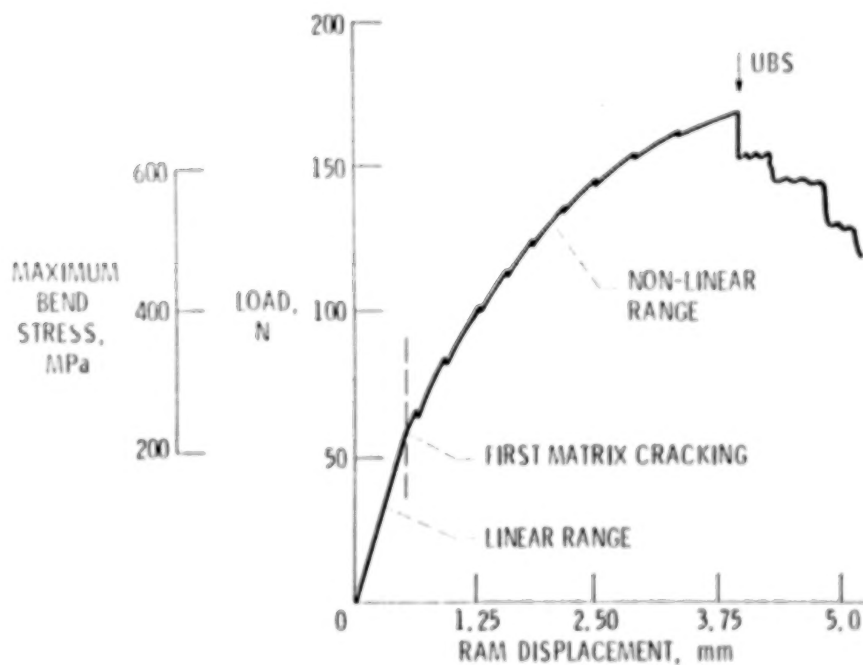
CS-86-0200

DENSITY AND POROSITY DATA FOR SiC /RBSN COMPOSITES

VOLUME FRACTION OF FIBERS	BEFORE NITRIDATION		AFTER NITRIDATION	
	DENSITY gm /cc	MATRIX POROSITY, %	DENSITY gm /cc	MATRIX POROSITY, %
0	1.56	35	1.98	37
23 ± 3	1.70	54	2.19	39
40 ± 2	1.90	51	2.36	40

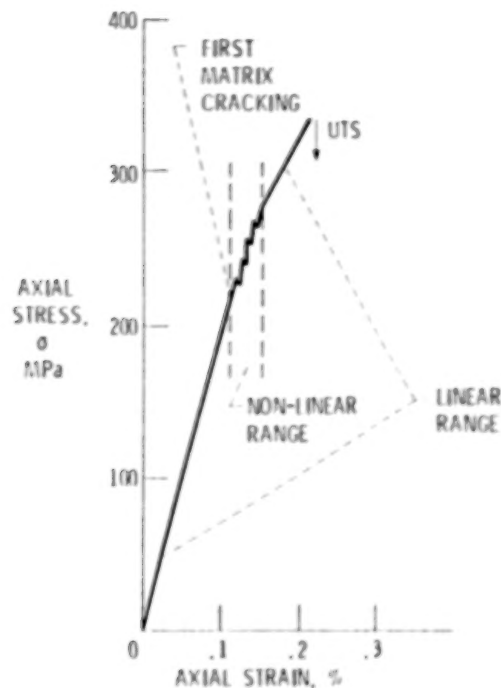
CD-85-16629

THE LOAD-DISPLACEMENT BEHAVIOR FOR 20 vol % SiC/RBSN COMPOSITE IN 3-POINT BENDING



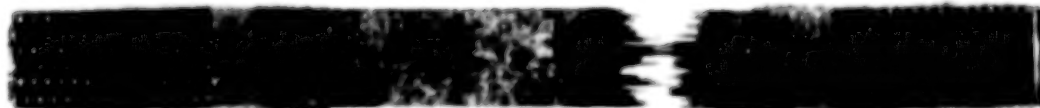
CS-85-2217

THE AXIAL STRESS-STRAIN BEHAVIOR FOR 20 vol %
SiC/RBSN COMPOSITE



125-100
CS 95-2220

FRACTURED TENSILE SPECIMEN OF SiC/RBSN COMPOSITE



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ROOM TEMPERATURE STRENGTHS OF SiC /RBSN COMPOSITE

TEST	AXIAL STRENGTH, MPa		
	0% FIBER	23 ± 3% FIBER	40 ± 2% FIBER
4 POINT BEND ($\frac{L}{h} = 15$) ^a	107 ± 26	539 ± 48	616 ± 36
4 POINT BEND ($\frac{L}{h} = 45$)	-----	675 ± 42	868 ± 32
3 POINT BEND ($\frac{L}{h} = 35$)	-----	717 ± 80	958 ± 45
TENSILE ^b	-----	352 ± 73	536 ± 20

^aTEST SPECIMEN HEIGHT ≈ 1.25 mm

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^bTEST GAUGE LENGTH 50 mm

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SiC /RBSN FRACTURE PARAMETERS

FIBER FRACTION, %	MATRIX CRACK SPACING, mm	INTERFACIAL SHEAR STRESS ^a , MPa	COMPOSITE STRESS AT WHICH MATRIX FIRST CRACKED, MPa	MATRIX FRACTURE STRAIN ^b
23 ± 3	2.0 ± 0.3	10.91	237 ± 25	0.0015
40 ± 2	0.9 ± 0.2	10.23	293 ± 15	0.0014

^aCALCULATED FROM ACK THEORY

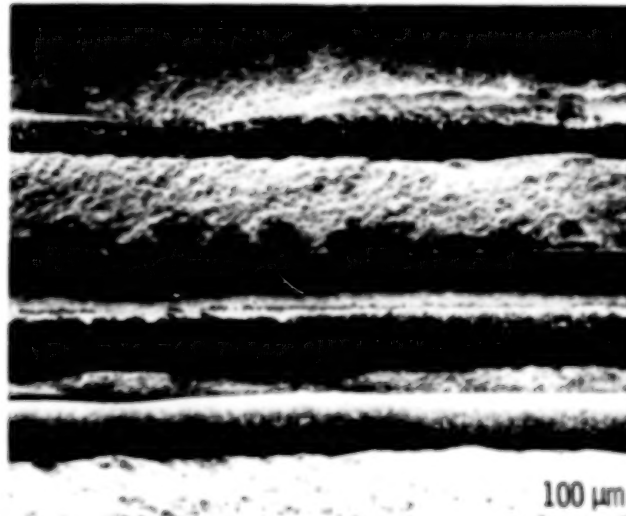
^bCALCULATED FROM ESTIMATED COMPOSITE MODULUS

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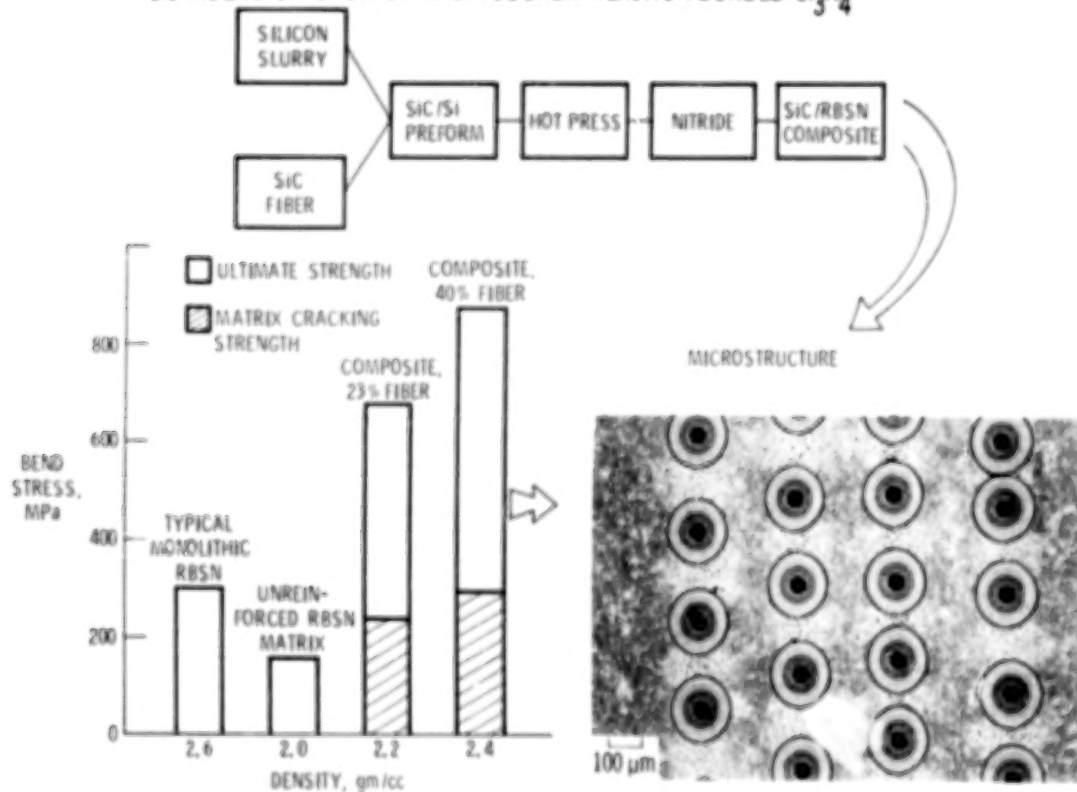
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FRACTURE SURFACE OF SiC/RBSN IN TRANSVERSE FLEXURE

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SiC FIBERS STRENGTHEN AND TOUGHEN REACTION-BONDED Si_3N_4



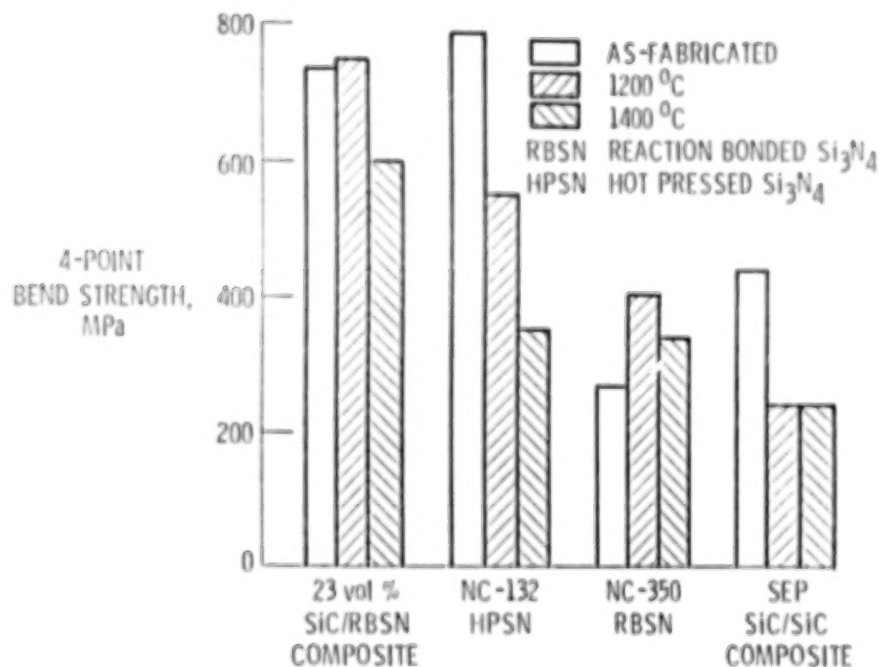
THERMAL STABILITY DATA FOR SiC/RBSN
AND SiC/SiC COMPOSITES

TREATMENT	ROOM TEMPERATURE AXIAL ULTIMATE STRENGTH, MPa	
	30 vol % SiC/RBSN	SEP SiC/SiC
AS-FABRICATED	350 ^a	441 ^b
1200 °C, 100 hr, AIR	316 ^a	234 ^b
1400 °C, 100 hr, AIR	323 ^a	234 ^b

a-TENSILE STRENGTH.

b-4-POINT BEND STRENGTH. (NO TENSILE DATA REPORTED. TENSILE STRENGTHS WOULD BE MUCH LOWER THAN 4-POINT BEND STRENGTH.)

ELEVATED TEMPERATURE STRENGTH (4-POINT BEND) FOR
SiC/RBSN COMPOSITE, MONOLITHIC SILICON-BASED CERAMICS, AND
SEP SiC/SiC COMPOSITE



SUMMARY OF RESULTS

- A STRONG AND TOUGH CERAMIC MATRIX COMPOSITE CAN BE FABRICATED BY REINFORCING RBSN BY HIGH MODULUS, HIGH STRENGTH CONTINUOUS LENGTH CVD SiC FIBER
- REINFORCEMENT OF RBSN BY CVD SiC FIBERS ALSO MEASURABLY INCREASES COMPOSITE MODULUS AND THE COMPOSITE STRESS AT WHICH MATRIX CRACKS
- WEAK FIBER-MATRIX BONDING ALLOWS MULTIPLE CRACKING AND GRACEFUL FAILURE
- COMPOSITE IS THERMALLY STABLE AND HAS BETTER ELEVATED TEMPERATURE STRENGTH THAN MANY COMMERCIALY AVAILABLE MONOLITHIC CERAMICS
- FURTHER IMPROVEMENTS IN COMPOSITE PROPERTIES ARE POSSIBLE WITH
 - INCREASE IN MATRIX STRENGTH (DECREASE IN POROSITY)
 - SMALL DIAMETER FIBERS
 - FIBER COATING

CURRENT AND FUTURE STUDIES

CURRENT:

- OPTIMIZATION OF PROCESSING VARIABLES
- POST FABRICATION TREATMENTS
- LAMINATE PROPERTIES ($0^0/90^0$, $0^0/90^0/45^0$)
- INTERFACIAL REACTION KINETICS

FUTURE:

- MEASUREMENT OF ELEVATED TEMPERATURE TENSILE STRENGTH AND STRESS RUPTURE DATA
- THERMAL PROPERTIES
- OXIDATION

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16. Abstract This publication is a compilation of abstracts and slides of papers presented at the NASA Lewis Structural Ceramics Workshop held at the Sheraton Hopkins Hotel, Cleveland, Ohio, on May 20 and 21, 1986. Collectively, these papers depict the scope of NASA Lewis' structural ceramics program. Each paper provides a brief overview of a technical area in which NASA Lewis Research Center has a significant research focus. The technical areas include monolithic SiC and Si ₃ N ₄ development, ceramic matrix composites, tribology, design methodology, nondestructive evaluation (NDE), fracture mechanics, and corrosion.			
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